HUNGARICA ACTA CHIMICA

AUCTORITATE

ACADEMIAE SCIENTIARUM HUNGARICAE

EDIDIT

ZOLTÁN CSŰRÖS

VOL. I., NO. 4—5.

BUDAPESTINI

MCMXLIX

The HUNGARICA ACTA CHIMICA are being published by the *Hungarian Academy of Sciences* in Budapest, edited by Prof. Zoltán Csűrös (Budapest).

The HUNGARICA ACTA CHIMICA will be issued in fascicles not tied to any fixed dates; 6 fascicles will go to a volume. The HUNGARICA ACTA CHIMICA are obtainable through all booksellers.

Manuscripts in a form ready for printing should be sent to the Editor. Prof. Z. Csűrös, Budapest, XI., Műegyetem-rakpart 3. Only papers not published as yet elsewhere, written in English, French or German, and dealing with subjects belonging to the field of Chemistry or to neighbouring fields will be accepted for publication. Every paper should contain a short summary, indicating particularly the points the author considers as constituting his own new results and thereby as representing the items of scientific progress achieved due to his work.

Of their papers to be published, authors will receive galley-proofs. Subsequent alterations of text, in so far as they exceed 10% of the typesetting cost, will be charged to the author.

Authors will receive 100 reprints of their papers free of cost.

THE ADMINISTRATION OF THE ACADEMY
Budapest, V., Akadémia-utca 2.

HUNGARICA ACTA CHIMICA, éditées par *l'Académie Hongroise des Sciences* de Budapest, sont dirigées par M. Zoltán Csűrös, professeur à l'École Polytéchnique de Budapest.

HUNGARICA ACTA CHIMICA apparaîssent périodiquement; six fascicules forment un volume. HUNGARICA ACTA CHIMICA sont accessibles par chaque librairie.

Les manuscrits prêts à tirer en anglais, en français ou en allemand doivent être envoyés à M. Z. Csűrös, professeur à l'École Polytéchnique de Budapest, XI., Műegyetem-rakpart 3.

Des oeuvres inédites du domaine de la chimie et des sciences apparentées y seront admises. Chaque ouvrage doit comporter son court résumé, contenant surtout les faits essentiels, considérés par l'auteur comme ses propres résultats, et comme un progrès scientifique obtenu par son activité.

Les auteurs reçoivent l'épreuve de leur ouvrage. Si les frais des changements ultérieurs du texte dépassent 10% des frais de composition, ils seront supportés par l'auteur.

Les auteurs reçoivent de leur ouvrage à titre gratuit 100 tirages.

L'ADMINISTRATION DE L'ACADÉMIE
Budapest, V., Akadémia-utca 2.

Die HUNGARICA ACTA CHIMICA werden durch die *Ungarische Akademie der Wissenschaften* in Budapest herausgegeben und von Prof. Zoltán Csűrös (Budapest) redigiert.

Die HUNGARICA ACTA CHIMICA erscheinen zwangslos in Heften; 6 Hefte bilden einen Band. Die HUNGARICA ACTA CHIMICA sind durch jede Buchhandlung zu beziehen.

Druckfertige Manuskripte sind an Prof. Dr. Z. Csűrös, Budapest, XI., Műegyetem-rakpart 3. zu senden. Aufgenommen werden Arbeiten in englischer, französicher oder deutscher Sprache aus dem Gebiet der Chemie und aus den Nachbargebieten, die vorher nicht veröffentlicht wurden. Jede Arbeit soll eine kurze Zusammenfassung enthalten, in welcher vor allem die Punkte angegeben sind, welche der Verfasser als seine neuen Ergebnisse und damit als den durch seine Arbeit erzielten wissentschaftlichen Fortschritt betrachtet.

Die Verfasser erhalten von ihren Arbeiten eine Fahnenkorrektur. Nachträgliche Textänderungen werden, soweit sie 10% der Satzkosten übersteigen, den Verfassern in Rechnung gestellt.

Die Verfasser erhalten von ihren Arbeiten 100 Sonderdrucke unentgeltlich.

DIE GESCHÄFTSFÜHRUNG DER AKADEMIE
Budapest, V., Akadémia-utca 2.

INVESTIGATIONS ON CATALYSTS. III:[1] EFFECT OF THE AMOUNT OF PALLADIUM AND PLATINUM CATALYSTS ON THE RATE OF HYDROGENATION OF ETHYLENE-CARBOXYLIC ACIDS.

BY ZOLTÁN CSŰRÖS AND EDITH GERGELY, NÉE POPPER.
(ORG.-CHEM. TECHNOLOGICAL INSTITUTE OF THE TECHNICAL UNIVERSITY, BUDAPEST).

RECEIVED : 18. III. 1947.

While heterogeneous catalysis has been thoroughly studied, few investigations were made so far to explain the influence of the amount of catalysts on the rate of a reaction. The scattered references found in literature are very often contradictory. According to some of the authors (1, 2) the rate of reaction increases rapidly with the amount of the catalyst, but not proportionally to it. According to other data (3), the rate of reaction is proportional to the amount of the catalyst. *Salkind* states: "The rate of hydrogenation of triple-bonded glycols is generally proportional to the amount of the colloidal palladium catalyst employed, but contrary to all expectations it is in some cases independent of the same." (4). If we examine the experimental basis of these statements, we mostly discover that the authors based their conclusions on the results of experiment performed with two or three amounts of the catalyst only.

This problem was systematically explored first by *Kailan* and *Hartel* (5). They hydrogenated oleic acid with various amounts of nickel catalyst and found that rate-constants were growing at the beginning with increasing concentration of the catalyst and then decreasing thus describing a maximum graph.

Hydrogenation series of *Csűrös, Zech* and *Géczy* (6) and later of *Csűrös, Zech* and *Pfliegel* (7) employing various amounts of catalysts

[1] See:
I.: *Csűrös, Z., Zech, K.* and *Géczy, I.*, Selective hydrogenation by means of catalysts, I: The hydrogenation of cis-trans isomers with varying quantities of catalyst (colloidal palladium) and selective hydrogenation of unsaturated carbonyl compounds with the aid of promoters. Hungarica Acta Chimica *1*, 1 (1946).
II.: *Csűrös, Z., Zech, K.* and *Pfliegel, T.*, Selective hydrogenation by means of catalysts, II.: The hydrogenation of α, β-unsaturated carbonyl compounds by means of varying quantities of catalyst (colloidal palladium). Hungarica Acta Chimica *1*, 24 (1946).

(colloidal palladium or palladium precipitated on $BaSO_4$) revealed, that when hydrogenating dissolved unsaturated compounds the rate of hydrogenation increases at the beginning with increasing amount of the catalyst, reaches a local maximum, afterwards decreases down to a local minimum and then increases again. This phenomenon was interpreted by *Csűrös, Zech* and *Géczy* by supposing that the active surface of the catalyst very likely did not grow proportionally to the amount of the catalyst.

The purpose of our recent experiments was to ascertain as to whether the minimum-maximum character of the graphs of hydrogenation-time[2] observed in our former experiments was a specific singularity of the colloidal palladium and that of palladium precipitated on $BaSO_4$, or circumstances were alike with other catalysts too? Considering, that the catalytical reactions occur on the surface of the catalyst, the supposition was readily available, that the rate of reaction in the case of a catalyst of the same quality will be determined by the active surface of the catalyst. If that was right, the minimum-maximum graph could be explained by the increase of the total surface of the catalyst to a maximum with increasing concentration of the latter, followed by a decrease to a minimum and afterwards by a second increase, which tends towards a limit value. Changes of physical properties like that we mostly find in colloidal systems. A minimum-maximum graph of hydrogenation-time was observed hitherto only with colloidal palladium and such one precipitated on $BaSO_4$, the latter consisting of very small crystalls and consequently being apt to change its surface by re-crystallisation. Therefore it seemed first of all necessary to examine catalysts, which were not colloids and the carriers of which were not at all soluble in the solvent employed as a medium of hydrogenation. Palladium and platinum catalysts precipitated on bone-black proved to be suitable for this purpose.

We hydrogenated some ethylene-carboxylic acids (cinnamic, fumaric, maleic, mesaconic, citraconic, tiglic and angelic acids) in solutions of identical volumes and mol-concentrations with different amounts of colloidal palladium and platinum catalysts and such ones precipitated on bone-black and we received in all cases hydrogenation-time graphs of minimum-maximum character. (See figures 1, 3, 4, 5, 6.)

Thus we have proved on the one hand that minimum-maximum graphs of our former experiments were not caused by the colloidal character of the catalysts and on the other hand that this minimum-maximum graph represents a relationship of general validity for all hydrogenation reactions,

[2] The *hydrogenation-time graph* describes the relationship between the amount of the catalyst and the relating time of hydrogenation. It must not be mistaken with a graph describing the progress of a hydrogenation reaction in time.

where hydrogen, the substance to be hydrogenated and the catalyst were present in three separate phases.

In our further experiments we have also measured hydrogen adsorption of the catalysts suspended in solvents employed for hydrogenations.

The high adsorptive capacity of *Pd* and *Pt* is well-known. Hydrogen may be adsorbed besides real adsorption by *van der Waals*-forces also by chemisorption (8) and by dissolution (9). We have to consider the simultaneous effect of all of these three phenomena at room temperature. To these three must be added in case of supported catalysts the hydrogen-adsorption of the carrier and in case of colloidal catalysts the effect of the protective colloid modifying circumstances of adsorption. As catalysts were suspended also in solvent, lyosorption of the same might have also changed the H_2-adsorptive ability of the catalyst. We could, however, measure only the resultant of all these complicated and partly contrasting effects, which we shall call henceforth *hydrogen-adsorption* of the catalyst, considering, that not only real adsorption is involved in this expression.

According to data available in literature hydrogen-adsorption of the same amount of catalyst was hitherto generally examined as a function of outside circumstances, like pressure, temperature. Though *Maxted* (10) has measured hydrogen-adsorption of varying amounts of catalysts too, he employed them dry and thus his measurements are not comparable with our results.

We found no data in the literature concerning the hydrogen-adsorption of varying amounts of catalysts suspended in a liquid and generally concerning the amount of gas adsorbed by any adsorbent suspended in a liquid either.

Some analogy seems to appear in the measurements, which examine the relation of the amount of adsorbent to the adsorption of a substance dissolved in a solvent. The results of these measurements may be described by the adsorption-isotherms of *Kroeker*. According to this the relative adsorbed amount changes with the amount of the adsorbent along a hyperbola graph. It is, however, evident that the circumstances in our measurements are different. In the former case concentration of the adsorbed substance decreases in the solution by approaching the adsorption equilibrium. In our measurements, however, pressure of hydrogen reamains constant. It is of interest though, to mention, that *Ostwald* and coworkers proved, that very often anomalies may be observed on adsorption-isotherms of *Kroeker* and the relation of the amount of adsorbed substance to that of the adsorbent may be described by maximum graphs or even by maximum-minimum graphs (11, 12, 13, 14).

Adsorption of hydrogen did not increase linearly with the amount of catalyst in our experiments either. Plotting the amount of hydrogen adsorbed by a unite part of the catalyst, i. e. the relative hydrogen adsorption against the amount of catalyst we received similar curves passing through a minimum and maximum and afterwards converging to a limit value in the case of all catalysts examined. (See figures 2, 3, 4, 5, 6.).[1]

There is a close relation between adsorption graphs and hydrogenation-time graphs. The relation is especially marked in the case of catalysts precipitated on bone-black. The adsorption graphs and hydrogenation-time graphs of ethylene-carboxylic acids with trans configuration run for example nearly parallel in the case of *Pd* catalyst on bone-black and their extreme values appear at identical amounts of the catalyst. (Figure 3). The hydrogenation-time graphs of cis compounds are displaced as to those of the trans type so that their minimum coincides with the maximum of the adsorption graph at identical amounts of the catalyst, Thus it is of high interest, that the optimal quantity of *Pd* catalyst for hydrogenation of trans compounds is able to adsorb relatively the smallest amount of hydrogen. On the other hand compounds with cis configuration may be hydrogenated fastest by the amount of catalyst having the highest H_2-adsorption. There is evidence, that hydrogenation-time graphs of cis and trans compounds respectively run nearly parallel within the respective types and their extreme values appear at identical amounts of the catalyst. The relationship of adsorption graph and hydrogenation-time graph offers a convenient method for selective hydrogenation of cis-trans isomers. Having the adsorption graph of a catalyst we may establish its amount which will be enable us to hydrogenate a chosen component of a mixture containing cis-trans isomers, in the most selective way. By this experiments we have also confirmed the statement of *Csűrös, Zech* and *Géczy* (6), that *Paal'* s rule — according to which the cis modification is always hydrogenated faster out of cis-trans isomers by *Pd* catalyst (15, 16) — is only correct within narrow concentration limits of the catalyst. Applying concentrations of the catalyst below or above these limits — on the contrary — the trans type of the compound may be hydrogenated faster.

There is a close relationship between the adsorption-graph and the hydrogenation-time graph in the case of *Pt* catalyst on bone-black just as well, but the compounds of cis and trans configuration change parts. Here hydrogenation-time graphs of the cis compounds run nearly parallel to the adsorption graph and the graphs of the trans types are displaced.

[1] This curve will be cited in this paper as *adsorption-graph.*

Thus in contrary to *Pd*, cis compounds of ethylene-derivatives are hydrogenated faster (Figure 5) by amounts of *Pt* catalyst adsorbing relatively the smallest amount of hydrogen, while trans isomers may be hydrogenated faster by amounts of catalysts of relatively highest adsorption. From the displacement of the graphs also follows, that — again contrary to *Pd* — by large and small amounts of *Pt* catalyst the cis modification, whereas by medium amounts the trans type may be hydrogenated faster.

We also observed another contrast between hydrogenation properties of *Pd* and *Pt* catalysts prepared in the same way. Succession of hydrogenation-rate of ethylene-carboxylic acids of the same configuration is also different with the two noble metals as shown in Table XII. (It must be mentioned, that only compounds of identical configuration, the hydrogenation-time graphs of which are nearly parallel and are not crossing each other, may be compared in this way).

From this contrasts the conclusion may be drown, that hydrogenation reactions occur according to different mechanisms on the surface of the two noble metals.

In the case of colloidal *Pd* and *Pt* catalysts the relative position of the hydrogenation-time graphs of isomers is the same as that established by corresponding catalysts on bone-black. But the limit values of hydrogenation time graphs of the same compound do not coincide and the graphs are generally not parallel to the adsorption graph. Here the protective colloid very likely still complicates surface conditions.

It was remarkable, that — though colloidal catalysts adsorbed essentially less hydrogen, then the ones precipitated on bone-black — desorption of hydrogen caused by adsorption of the substance to be hydrogenated was higher also in its absolute value from colloidal catalysts then those precipitated on bone-black. (See notes below tables). Only fumaric acid of trans type caused no considerable desorption from the colloidal *Pd* catalyst and — as seen in Figure 4 — its hydrogenation-time graph is nearly parallel to the adsorption graph as well as in the case of *Pd* catalyst on bone-black.

Here arises the question as to why does rate of hydrogenation decrease or increase with lower or higher H_2-adsorption of one or the other amount of the catalyst? Whether the amount of adsorbed hydrogen exerts any direct influence or we only may draw conclusions from the adsorptive ability of the catalyst upon the structure of its surface, which is advantageous or disadvantageous for catalysing the reaction investigated.

If the first statement was right, by means of it could interprete the irregularities occured on colloidal catalysts. Hydrogen desorption effected by substance to be hydrogenated is so small compared with high H_2-

adsorption of catalysts on bone-black, that differences arising between them may be practically neglected. That means, that the same amount of hydrogen remains on the surface of the catalyst while hydrogenating different substances. The difference between desorptions effected by different substances may be, however, by no means neglected working with colloidal catalysts of low hydrogen adsorption, thus hydrogenation-time graphs of ethylene-carboxylic acids of identical type may also be displaced from one another.

On the other hand former experiences concerning the mechanism of catalysed reactions, according to which reactions can be performed only on scattered points, on the so called "active centers" of catalysts (17, 18, 19, 20) call for the second supposition. Without considering which of these two suppositions is right, it is undoubtful, that a close relationship exists between the adsorption graphs and hydrogenation-time graphs, as it was proved by our further experiments, too.

We hydrogenated cinnamic acid with different amounts of the same palladium catalyst prepared previously on bone-black and during saturation of the catalyst with hydrogen and also in the course of hydrogenation reaction we have stirred the suspension in one series very quickly, while in the other series slower. Comparison of the two series showed as a result, that the extreme values of the hydrogenation-time graph and those of the adsorption graph appeared at smaller amounts of catalysts, when stirred slower, than in the case when stirring was quick and the graphs — especially the adsorption graph — were flatter (Figure 7). But adsorption graph and hydrogenation-time graph were displaced together when intensity of stirring was changed and their minimum and maximum respectively was reached at identical amounts of the catalysts.

Before giving the theoretical interpretation of these experiences we should like to discuss first the latest results of *Matthews* (21). He measured the decrease of interfacial tension between water and cyclohexane effected by methyl cellulose and found that interfacial tension was smaller some minutes after addition of methyl cellulose than some hours later, when equilibrium was already established. That is to say that surface tension changed with time along a graph having a minimum. Increasing the amounts of methyl cellulose, the minima of graphs were displaced towards steadily decreasing times till at last with the largest amount equilibrium was reached so quickly, that he could not observe the eventual minimum. Having measured surface tensions belonging to various concentrations of methyl cellulose at one minute, two minutes and longer time after adding the same, he observed, that surface tension of the system one or two minutes old changed with concentration of methyl cellulose along a graph

passing through a minimum and maximum, while an older system gave a hyperbola as expressed by the adsorption isotherm of *Gibbs*. The graph of systems two minutes old was, however, much flatter than this of one minute of age and its minimum and maximum were at lower concentrations of methyl cellulose. The minimum-maximum graphs were thus caused by the systems having not reached an equilibrium.

The minimum-maximum graphs of our experiments received when stirring was fast flattened out as soon as stirring became slower and their extreme values were displaced in the same manner as in experiments of *Matthews*. Between these two phenomena there may exists also a closer relationship than the mere agreement of the shape of the graphs.

According to the adsorption isotherm of *Gibbs* adsorptive capacity of a system is the function of its surface tension. Thus adsorptive capacity of a system being not in equilibrium may also show some irregularities.

Hydrogen adsorption of the catalyst was measured by suspending the catalyst on bone-black of high porosity in small volume of a liquid and stirring the suspension in an atmosphere of hydrogen. The small particles of the catalyst may aggregate and again disaggregate as a consequence of stirring and thus new surfaces may steadily arise and disappear. Consequently there is no possibility of reaching a lyosorptive equilibrium between the catalyst and the solvent, i. e. we have measured H_2-adsorption in systems of non-equilibrium position. We have seen that when stirred slowly, graphs flattened out, just like as in the experiments of *Matthews* in older systems near to the equilibrium. It may be supposed, that if reaction mixtures were not at all stirred minima and maxima of the adsorption graph and those of the hydrogenation-time graphs would totally disappear, just like in the experiments of *Matthews*, when the systems were in equilibrium.

In failure of suitable equipment we did not succeed in solving this problem as yet. But even if it were proved, that minimum-maximum character of the graphs was caused only by stirring, that would not at all change the practical value of the phenomenon as contact catalytic reactions, where one component of the substrate is gaseous, the other one a liquid, are accomplished to a measurable rate only by stirring or shaking.

SUMMARY.

1. We have demonstrated through many series of hydrogenations performed with several kinds of catalysts, that hydrogenation time changes with the amount of catalyst along a graph (hydrogenation-time graph) passing through a minimum and a maximum and tending towards an extreme value in all of the hydrogenation reactions, where H_2 is present

in the gas phase, the substance to be hydrogenated is dissolved in a liquid and the catalyst, however, in the solid phase or in colloidal suspension.

2. Relative adsorption of hydrogen on colloidal catalysts or on those suspended in a solvent changes just as well with the amount of the catalyst along a minimum-maximum graph (adsorption graph).

3. Hydrogenation-time graph of olefins are determined by adsorption graph of catalysts precipitated on bone-black as follows:

a) Minima and maxima of adsorption graph of palladium catalyst precipitated on bone-black and those of the hydrogenation-time graphs of ethylene-derivatives with trans configuration appear at identical amounts of the catalyst, the minima of graphs of cis compounds, however, coincide with the maxima of the adsorption graph at the same amount of the catalyst.

b) On the contrary with platinum catalyst precipitated on bone-black extreme values of the hydrogenation-time graphs of cis compounds coincide with the corresponding points of the adsorption graph at identical amounts of catalysts and the graphs of trans compounds are displaced in the way mentioned above.

4. Hydrogenation-time graphs of ethylene-derivatives having identical configuration, run nearly parallel with catalysts on bone-black and their corresponding extreme values appear at identical amounts of the catalysts.

5. In case of colloidal catalysts extreme values of hydrogenation-time graphs of compounds of identical type do not appear at identical amounts of catalysts and the graphs are generally not parallel to adsorption graphs either. This anomaly may be very likely attributed to the effect of the protective colloid.

6. Out of the cis-trans ethylene-derivatives:

a) with small and large amounts of palladium catalysts the trans types, with medium amounts cis types of the compounds,

b) with small and large amounts of platinum catalysts the cis types, with medium amounts the trans types of the compounds may be hydrogenated faster.

7. With palladium catalysts even the succession of the rate of hydrogenation of identical types of compounds differs from that, when platinum catalysts are employed. On the basis of these differences and of those discussed under 3. and 6. it might be supposed that hydrogenation reactions occur according to different mechanisms on the surface of the two noble metals.

8. While studying the effect of the velocity of stirring we have ascertained, that the adsorption graph and the hydrogenation-time graph

are flatter in the case of slow, than in that of fast stirring, and their extreme values appear at lower amounts of the catalyst. The two graphs are displaced together, their maxima and minima respectively appear at identical amounts of the catalysts.

The minimum-maximum character of the graphs may be possibly caused by carrying out saturation of the catalyst and also the hydrogenation reaction by stirring.

EXPERIMENTAL PART.

As the purpose of our experiments was to ascertain as to how the rate of hydrogenation reactions and H_2-adsorption of the catalyst depends upon the amount of the latter, we have carried out all of our experiments strictly by the same method and varied only the amount of the catalyst.

A) *Experimental equipment.*

We carried out our experiments in semi micro hydrogenation apparatus used by *Csűrös, Zech* and *Géczy* (6) and improved by *Csűrös, Zech* and *Pfliegel* (7), (See Figure 8).

Saturation of the catalyst by hydrogen and hydrogenation itself is performed in flask *L*, which joins gasburette *B* by means of ground joint *CS*. The burette is connected on the one hand with levelling bulb *N* and on the other hand by means of stopcock C_1 with the Deville-bottle containing hydrogen. The gasburette broadening out downwards is graduated into 30 ml to an accuracy of 0,1 ml and on its upper part there is a stopcock (C_2) with an *L*-shaped boring, wich connects the hydrogenating flask and the gasburette (Position I.) or closing the gasburette connects the hydrogenating flask and the evacuating apparatus by means of tube *V* (Position II.). The hydrogenating flask is connected also with receptacle *T*, to be separated by means of stopcock C_3. The receptacle serves as a reservoir of the substance to be hydrogenated being kept separately from the catalyst already in a hydrogen atmosphere, while the catalyst is being saturated by hydrogen. Under the hydrogenating flask there is a magnet *M* which may be rotated by means of an electromotor and rotates the ironrod *K* welded into a glasstube inside the hydrogenating flask thus mixing the content of the flask in hydrogen atmosphere.

B) *Performance of experiments.*

The catalyst and one part of the solvent were placed into the hydrogenating flask. The substance to be hydrogenated was dissolved in the remaining part of the solvent and let to flow into receptacle *T*. After having

inserted the glass stoppers into the apparatus, the same was evacuated. Then turning stopcock C_2 into position I., hydrogen was passed from the gasburette into the apparatus. This procedure was repeated four times and finally the level was adjusted to the 0 point of the gasburette.

After reading the level with 0,01 ml accuracy, we started stirring, thus began *adsorption* of hydrogen by the catalyst. When the level of the gas did not rise anymore within five minutes, showing, that the catalyst is unable to consume hydrogen anymore, we read the level again. The difference of the two readings gave the amount of hydrogen necessary for saturation of the catalyst by stirring.

The level was adjusted to 0 point again and after reading, the substance to be hydrogenated was let to flow into the flask by opening stopcock C_3. The level sank due to hydrogen desorption caused by adsorption of the substance to be hydrogenated. We quickly noted the level and so received our data concerning the desorption of hydrogen. At the same time we started measuring the *time of hydrogenation.*

All of our experiments were carried out at room temperature, i. e. at 20—22° C and under atmospheric pressure.

Volume of the liquid was 15 ml at saturation of the catalyst with hydrogen. Catalysts on bone-black were always suspended in a mixture of 10 ml alcohol and 5 ml distilled water and the volume of colloidal catalysts was filled up to 15 ml with distilled water.

The substance to be hydrogenated was brought into the apparatus always in a solution of 5 ml volume. The solvent was alcohol in the case of catalysts on bone-black and water in case of colloidal catalysts, but in this latter case ethylene-carboxylic acids were neutralised with soda ash. At all times 0,001 mol substance was hydrogenated. Samples were measured by making a 0,2 mol standard solution, 5 ml of which contained just 0,001 mol of the substance.

On the basis of calculations 24,3 ml of hydrogen should be consumed at room temperature for saturation of 0,001 mol substance. Generally a little more, than that was consumed due very likely to side-reactions. As we were interested in the main reaction, we have taken into account the time-limits necessary for consuming 24 ml of hydrogen and calculated hydrogenation rates based upon these values.

We took particular care of uniform stirring at all times. We received really comparable results even under identical experimental conditions only if we have been employing catalyst neither the adsorptive capacity nor the catalytic activity of which were changing considerably during the time necessary for completing the series to be compared. Properties of the colloidal catalysts mentioned above were constant for 2—3 weeks after

their preparation. Activity of catalysts on bone-black, but especially their adsorptive capacity were fluctuating very much during the days following their preparation, therefore we have employed them only 3—4 weeks later when fluctuations no more exceeded the accuracy of the measurements (± 5%). Activity of catalysts was controlled daily by repeating one of the former experiments.

It must be mentioned, that we have never been able to reproduce catalysts of totally identical activity and especially of identical adsorptive capacity. Therefore correlated series were always performed with the same catalysts, which were prepared for that reason in large quantity.

C) *Preparation of catalysts.*

1. *Palladium catalyst precipitated on bone-black* (22).

10 grams of bone-black and about 150 ml distilled water were brought into a hydrogenation flask put on a shaking machine and the apparatus was rinsed with hydrogen. When the gas leaving the outlet did not give anymore the explosion test, a solution of 1 gram $PdCl_2$ in 50 ml 0,2 *N* hydrochloric acid was added by drops by means of a dropping funnel inserted into the flask. The catalyst was shaken for 30—35 minutes in a hydrogen atmosphere, then brought on a filter, washed with distilled water till it became acid-free and then rinsed with some alcohol and ether. It was kept for 24 hours in vacuum, the vacuum desiccator was opened letting in CO_2. The catalyst was put quickly into a glass container with a well fitting stopper. (5,66 mg *Pd*/0,1 g).

2. *Colloidal Pd catalyst* (23).

0,5 g $PdCl_2$ was dissolved in 80 ml distilled water, which was kept between 70—80° C until $PdCl_2$ was totally dissolved. The solution was heated to boiling and 10 ml of a hot 5% solution of arabic gum was added. The solution was poured still hot into a shaking bottle and after having displaced air by hydrogen it was shaked in a H_2 atmosphere for half an hour. The black, in thin layer browny translucent colloidal solution was filled up to 100 ml precisely (3,002 mg *Pd*/ml).

3. *Pt catalyst precipitated on bone-black* ("A") (24).

10 grams of bone-black were suspended in a small amount of water then a concentrated solution of 1,72 g H_2PtCl_6 in water was added. It was stirred for three hours on a water bath of 50° C, cooled, then made alkaline with a concentrated solution of sodium carbonate. A solution

of hydrazine hydrate was then added by drops to the suspension by means of a dropping funnel until a surplus of hydrazine hydrate was observed by means of a $KMnO_4$ droptest. Afterwards it was stirred for three hours on a water bath of 50° C, filtered, washed until free of chloride ions and alcalies, rinsed with alcohol and ether. Then it was kept for a night in a desiccator containing *CaO*. (*Pt* content 7,51 mg/0,1 g).

Pt catalyst precipitated on bone-black ("B").

1,72 g H_2PtCl_6 was reduced on 10 g bone-black with hydrogen in the same way as mentioned in connection with *Pd* catalyst.

4. *Colloidal Pt catalyst* (25).

0,86 g H_2PtCl_6, 0,20 g *KOH* and 1 g arabic gum were dissolved in 100 ml distilled water and to the clear solution 1 g sodium carbonate dissolved in 20 ml water was added. This solution was boiled until the formerly orange-coloured colloidal $Pt(OH)_4$ became dark brown. Then it was dialysed for two days, at the end of which a further solution of 1 g of arabic gum in 20 ml water was added and after inoculation with a small amount of colloidal *Pd* it was shaken in a H_2 atmosphere for 45 minutes. Then the black, in thin layer browny translucent colloidal solution was filled up with distilled water to 200 ml (*Pt* content 2,047 mg/ml).

D) *Preparation of standard solutions.*

1. *For catalysts precipitated on bone-black.*

1,48 g cinnamic acid, 1,12 g citraconic anhydride, 1,30 g mesaconic acid, 0,98 g maleic anhydride, 1,16 g fumaric acid, 1,00 angelic acid or 1,00 g tiglic acid were dissolved in alcohol and then filled up exactly to 50 ml. 5 ml of the resulting solutions contained 0,001 mol ethylene-carboxylic acid.

2. *For colloidal catalysts.*

0,98 g	maleic anhydride	and	1,06 g	Na_2CO_3	
1,16 g	fumaric acid	„	1,06 g	„	
1,00 g	angelic „	„	0,53 g	„	or
1,00 g	tiglic „	„	0,53 g	„	

were dissolved in water and filled up to 50 ml exactly. The resulting solutions contained 0,001 mol ethylene-carboxylic acid in 5 ml.

E) *Results of measurements.*

H_2 adsorptive capacity of Pd catalyst on bone-black. (See Figure 2, 3.)

TABLE I.

Amount of catalyst, g	Amount of H_2 necessary for saturation of the catalyst, ml							Average, ml	Relative H_2 adsorption as related to 0,1 g catalyst, ml
0,10	3,30	3,55	3,35	3,40	3,65	3,70	3,50	3,50	3,50
0,20	5,05	5,20	5,10	5,20	5,40	5,45	5,30	5,24	2,62
0,30	4,10	4,25	4,00	4,10	4,35	4,30	3,95	4,14	1,38
0,35	2,90					3,15		3,02	0,86
0,40	5,40	5,60	5,30	5,45	5,70	5,50	5,25	5,46	1,38
0,50	8,60	9,00	8,85	8,95	9,10	8,80	8,50	8,90	1,78
0,60		8,65	8,30	8,45	8,50	8,30	8,15	8,39	1,38
0,70	9,10	9,30	8,85	9,00	9,20	8,95	9,20	9,08	1,30
1,00	12,30							12,30	1,23

Data in the same column are results of measurements made on the same day.

Hydrogenation with Pd catalyst precipitated on bone-black.
(See Figure 1, 3.)

Amount of catalyst, g	Hydrogenation-time till H_2-consumption amounts to		Hydrogenation-rate, ml/minute	Hydrogenation-time till H_2-consumption amounts to		Hydrogenation-rate, ml/minute
	12 ml	24 ml		12 ml	24 ml	
	minute			minute		
TABLE II. Cinnamic acid (trans):						
0,10	15,0	31,0	0,774			
0,20	12,5	26,0	0,923			
0,30	11,5	22,5	1,066			
0,35	11,0	22,0	1,090			
0,40	12,75	26,5	0,908			
0,50	18,0	37,0	0,650			
0,70	13,0	27,0	0,890			
1,00	13,0	26,5	0,908			
TABLE III. Mesaconic acid (trans):				Citraconic acid (cis):		
0,10	13,0	27,0	0,890	13,5	28,0	0.855
0,20	11,0	23,0	1,042	11,5	23,5	1,020
0,30	9,5	19,0	1,260	9,75	20,0	1,196
0,40	11,5	25,0	0,960	8,75	17,5	1,370
0,50	14,0	29,0	0,825	10,0	20,5	1,170
0,60	11,0	23,0	1,042	12,5	26,0	0,922
0,70	9,5	20,0	1,196	11,0	22,5	1,065
TABLE IV. Fumaric acid (trans):				Maleic acid (cis):		
0,10	25,0	52,0	0,459	25,5	53,0	0,454
0,20	22,25	47,0	0,507	24,0	49,0	0,490
0,30	20,5	42,0	0,572	21,5	43,0	0,558
0,40	21,0	42,5	0,566	19,5	39,5	0,608
0,50	21,75	44,5	0,539	23,0	46,5	0,516
0,60	19,0	39,0	0,616	20,5	42,0	0,572
0,70	17,25	36,5	0,668	18,25	37,5	0,640

Hydrogenation with Pd catalyst precipitated on bone-black.
(See Figure 1, 3.)

Amount of catalyst, g	Hydrogenation-time till H_2-consumption amounts to		Hydrogenation-rate ml/minute	Hydrogenation-time till H_2-consumption amounts to		Hydrogenation-rate, ml/minute
	12 ml	24 ml		12 ml	24 ml	
	minute			minute		
TABLE V.	Tiglic acid (trans):			Angelic acid (cis):		
0,10	69,0	144,0	0,167	47,5	97,0	0,248
0,20	39,5	81,0	0,296	38,0	79,0	0,302
0,30	30,0	61,5	0,390	33,5	68,0	0,352
0,35	28,0	58,0	0,415			
0,40	32,0	65,5	0,366	29,0	60,0	0,400
0,50	34,0	69,0	0,348	31,0	64,0	0,375
0,60	27,5	58,0	0,415	30,0	63,0	0,381
0,70	24,5	51,0	0,470	27,5	58,0	0,415

Desorptions varied with all substances between 0,00—0,15 ml.

TABLE VI.

Adsorptive capacity of colloidal Pd catalyst.
(See Figure 4.)

Amount of catalyst, ml	Amount of H_2 necessary for saturation of the catalyst, ml				Average, ml	Relative H_2-adsorption as related to 1 ml of catalyst, ml
1,0		0,32		0,38	0,35	0,35
2,0	0,40	0,50	0,47	0,43	0,45	0,225
3,0	0,50	0,52	0,45	0,53	0,50	0,166
4,0	0,82	0,75	0,85	0,77	0,80	0,200
5,0	0,94	0,90	0,87	0,92	0,91	0,182
6,0	1,00	1,06	1,10	1,07	1,06	0,178
7,0		1,27	1,20		1,23	0,176
8,0	1,40	1,40	1,41		1,40	0,175
10,0		1,70			1,70	0,170
12,0	1,92				1,92	0,160

Hydrogenations with colloidal Pd catalyst.
(See Figure 4.)

Amount of catalyst, ml	Hydrogenation-time till H_2-consumption amounts to		Hydrogenation-rate, ml/minute	Hydrogenation-time till H_2-consumption amounts to		Hydrogenation-rate, ml/minute
	12 ml	24 ml		12 ml	24 ml	
	minute			minute		
TABLE VII. Fumaric acid (trans):				Maleic acid (cis):		
1,0	115	240	0,010			
2,0	58	130	0,185	87	184	0,130
3,0	50	107	0,224	60	126	0,190
4,0	54	114	0,210	38	80	0,300
5,0	43	92	0,260	59	126	0,190
6,0	41	85	0,283	50	104	0,230
7,0	40	82	0,292			
8,0	38	78	0,308	39	82	0,292
9,0						
10,0	37	77	0,340			
12,0	36	74	0,358			
Desorptions varied for fumaric acid between 0,00—0,05 ml and for maleic acid between 0,5—1,0 ml.						
TABLE VIII. Tiglic acid (trans):				Angelic acid (cis):		
1,0	138	300	0,080			
2,0	66	138	0,174	222	480	0,050
3,0	73	152	0,158	148	320	0,075
4,0	64	134	0,179	69	144	0,167
5,0	49	104	0,230	59	122	0,197
6,0	47	98	0,245	79	166	0,145
7,0				70	146	0,164
8,0				62	132	0,182

Desorptions varied for tiglic acid between 0,10—0,40 ml and for angelic acid between 0,40—0,80 ml.

TABLE IX.

Hydrogen consumption by Pt catalyst precipitated on bone-black ("A").
(See Figure 5.)

Amount of catalyst, g	Amount of H_2 necessary for saturation of the catalyst, ml				Average, ml	Relative H_2 adsorption as related to 0,1 g catalyst, ml
0,10	4,50	4,30	4,70		4,50	4,50
0,20	6,60	6,20	6,75	6,60	6,60	3,30
0,30	7,35	6,80	7,40	7,20	7,22	2,41
0,40	12,20	11,80	12,50	11,50	12,00	3,00
0,50	11,90	12,70	13,20	12,40	12,60	2,52
0,60	14,55	13,80	14,90	14,10	14,30	2,38
0,70	16,60	16,90		16,00	16,50	2,35
1,00	23,10				23,10	2,31

Data in the same column are results of measurements made on the same day.

Hydrogenations with Pt catalyst precipitated on bone-black ("A").
(See Figure 5.)

Amount of catalyst, g	Hydrogenation-time till H_2-consumption amounts to (minute)		Hydrogenation-rate, ml/minute	Hydrogenation-time till H_2-consumption amounts to (minute)		Hydrogenation-rate, ml/minute
	12 ml	24 ml		12 ml	24 ml	
TABLE X.	Fumaric acid (trans):			Maleic acid (cis):		
0,10	70,0	150,0	0,160	45,0	92,0	0,261
0,20	52,0	114,0	0,210	34,5	71,0	0,338
0,30	41,0	84,0	0,286	29,25	60,0	0,400
0,40	29,0	61,0	0,394	38,0	77,0	0,311
0,50	35,0	71,0	0,338	21,5	43,5	0,550
0,60	30,0	62,0	0,388	20,0	41,0	0,585
0,70	28,0	57,0	0,420	19,0	39,0	0,615
1,00	24,0	48,0	0,500			
TABLE XI.	Tiglic acid (trans):			Angelic acid (cis):		
0,10				63,0	135,0	0,178
0,20	79,0	165,0	0,145	53,0	109,0	0,220
0,30	53,25	109,0	0,220	41,0	82,0	0,293
0,40	36,5	76,0	0,316	44,25	90,0	0,267
0,50	42,25	85,0	0,282	29,0	60,0	0,400
0,60	35,0	70,0	0,343	26,25	54,0	0,445
0,70	31,0	64,0	0,375			

Desorptions varied for all substances between 0,00—0,15.

Hydrogenations with catalyst precipitated on bone-black ("B"). These experiments were carried out for comparing the activity of catalysts with identical *Pt* content but prepared by other method and on the other hand of *Pd* and *Pt* catalysts prepared by the same method. Data as to *Pd* catalyst are identical with those at Tables II., III., IV. and V.

TABLE XII.

Substance to be hydrogenated	*Pt* precipitated on bone-black, ("*B*") 0,40 g			*Pd* precipitated on bone-black, 0,40 g		
	Hydrogenation-time till H_2-consumption amounts to (minute)		Hydrogenation-rate ml/minute	Hydrogenation-time till H_2-consumption amounts to (minute)		Hydrogenation-rate ml/minute
	12 ml	24 ml		12 ml	24 ml	
Mesaconic acid ...	48,5	102,0	0,235	11,5	25,0	0,960
Tiglic acid	38,0	77,5	0,310	32,0	65,0	0,366
Cinnamic acid	31,0	64,0	0,375	12,75	26,5	0,908
Fumaric acid	29,5	61,5	0,392	21,0	42,5	0,566

TABLE XIII.

H_2-consumption of colloidal Pt catalyst.
(See Figure 6.)

Amount of catalyst, ml	Amount of H_2 necessary for saturation of catalyst, ml			Average, ml	Relative H_2-adsorption as related to 1 ml of catalyst, ml
1,0		0,39		0,39	0,39
2,0	0,47	0,40		0,45	0,217
3,0	0,40			0,40	0,133
4,0	0,30	0,50		0,40	0,100
5,0	0,42	0,47	0,40	0,43	0,086
6,0	0,42	0,55		0,48	0,081
7,0	0,66	0,75	0,50	0,65	0,093
8,0	0,35	0,39		0,37	0,046
10,0	0,50	0,40	0,41	0,44	0,044
12,0		0,42		0,42	0,036

TABLE XIV.

Hydrogenations with colloidal Pt catalyst.
(See Figure 6.)

Amount of catalyst, ml	Hydrogenation-time till H_2-consumption amounts to		Hydrogenation-rate, ml/minute	Hydrogenation-time till H_2-consumption amounts to		Hydrogenation-rate, ml/minute
	12 ml	24 ml		12 ml	24 ml	
	minute			minute		
	Maleic acid (cis):			Fumaric acid (trans):		
1,0				185	400	0,060
2,0	90	200	0,120	105	234	0,103
3,0				90	195	0,123
4,0	68	144	0,167	78	167	0,143
5,0	60	128	0,188	69	145	0,164
6,0	65	136	0,176	64	139	0,172
7,0	69	145	0,165	60	131	0,182
8,0	66	139	0,173	62	131	0,182
10,0	59	124	0,194	74	159	0,150
12,0				63	133	0,180

Desorptions effected by fumaric acid were in many cases equal to the whole amount of adsorbed hydrogen, maleic acid caused desorption of 0,15 ml at the most.

Effect of velocity of stirring upon H_2-adsorption capacity and hydrogenation-time of Pd catalyst on bone-black.

In experiments below cinnamic acid was hydrogenated with *Pd* catalyst in a medium of water-alcohol. Volume at saturation of the catalyst with hydrogen was 10 ml (3,5 ml water, 6,5 ml alcohol) and in the course of hydrogenation 15 ml (+ 5 ml of a solution of 0,2 mol cinnamic acid in alcohol). Reaction mixture was stirred very fast in series I. and slower in series II.

TABLE XV.

Amount of catalyst, g	Amount of H_2 necessary for saturation of catalyst, ml		Hydrogenation-time until H_2-consumption amounts to		Hydrogenation-rate, ml/minute
	altogether	to 0,1 g	12 ml	24 ml	
			minute		
I. series. Fast stirring.					
0,05	1,55	3,10	25,5	52,0	0,461
0,10	2,60	2,60	18,0	36,5	0,657
0,20	3,40	1,70	15,5	32,0	0,750
0,25	3,60	1,45	14,5	30,0	0,800
0,35	5,90	1,70	15,5	32,0	0,750
0,40	8,10	2,25	16,0	33,0	0,726
0,50	13,00	2,60	17,0	34,5	0,716
0,60	7,20	1,20	14,75	30,0	0,800
II. series. Slow stirring.					
0,10	3,25	3,25	21,5	46,0	0,522
0,15	3,10	2,03	20,5	42,5	0,564
0,20	4,30	2,15	21,0	43,0	0,557
0,30	6,10	2,30	23,5	49,0	0,490
0,40	5,70	1,42	21,25	43,5	0,551
0,45	4,25	0,95	19,5	40,0	0,600

(See Figure 7.)

Figure I.

HYDROGENATION-TIME GRAPH OF CINNAMIC ACID
with Pd catalyst precipitated on bone-black.

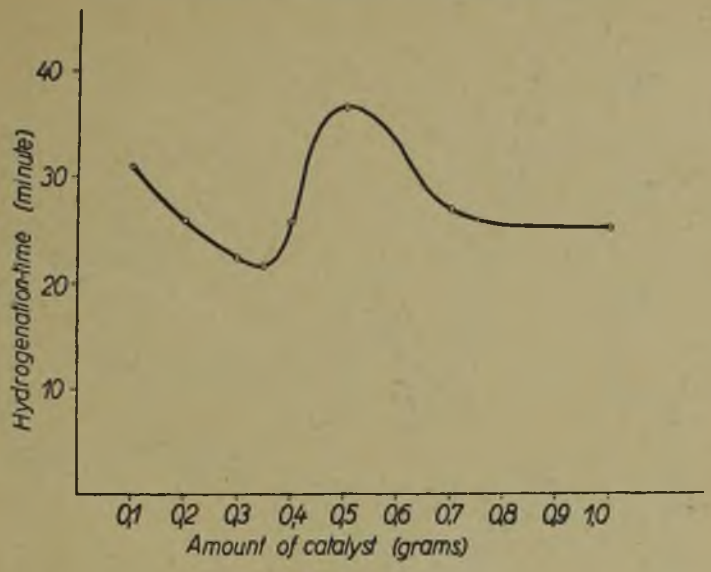


Figure II.

H_2-adsorption of Pd catalyst precipitated on bone-black, as related to 0.1 g catalyst

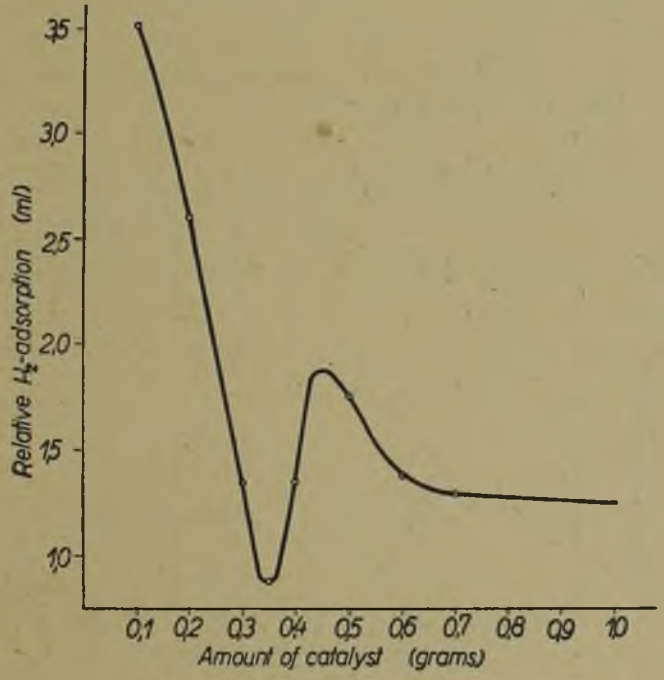
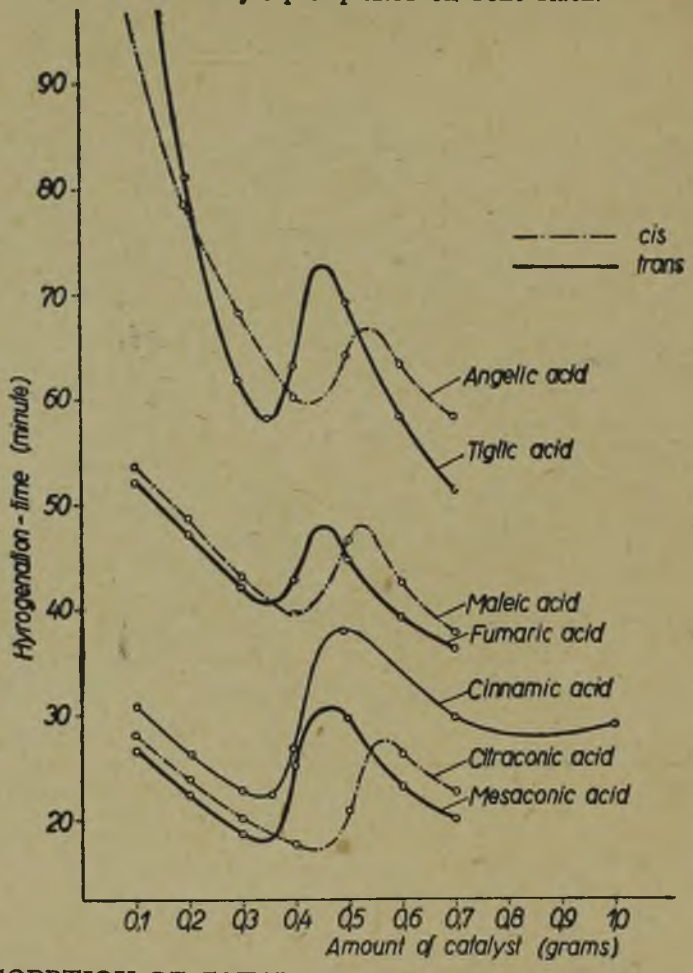


Figure III.

HYDROGENATION-TIME GRAPHS OF CIS-TRANS ISOMERS
with Pd catalyst precipitated on bone-black.



H_2-ADSORPTION OF CATALYST as related to 0,1 g of the catalyst.

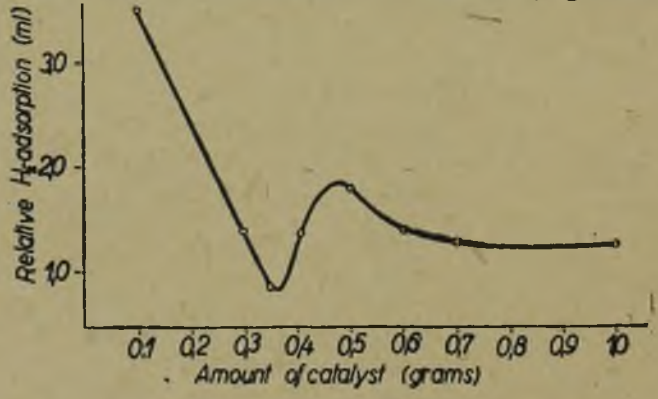
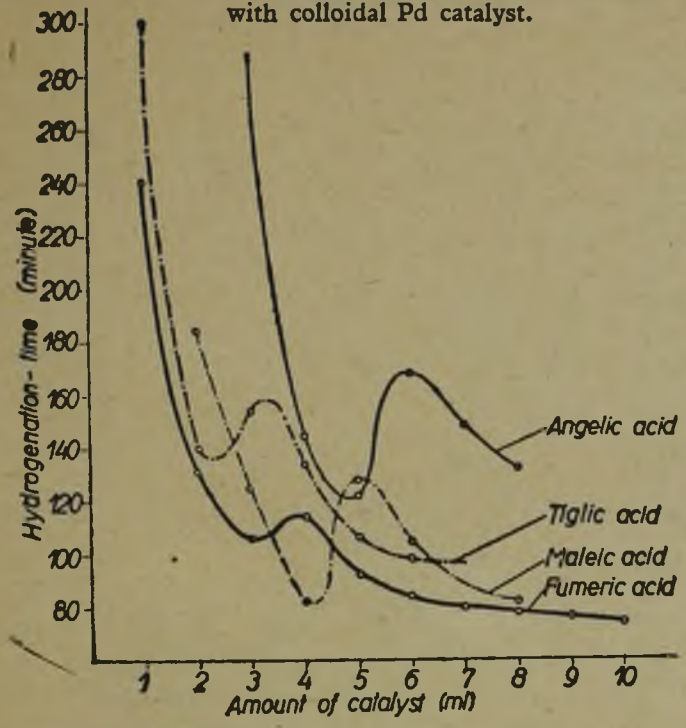


Figure IV.

HYDROGENATION-TIME GRAPHS OF CIS-TRANS ISOMERS with colloidal Pd catalyst.



H_2-ADSORPTION OF CATALYST as related to 1 ml of the catalyst.

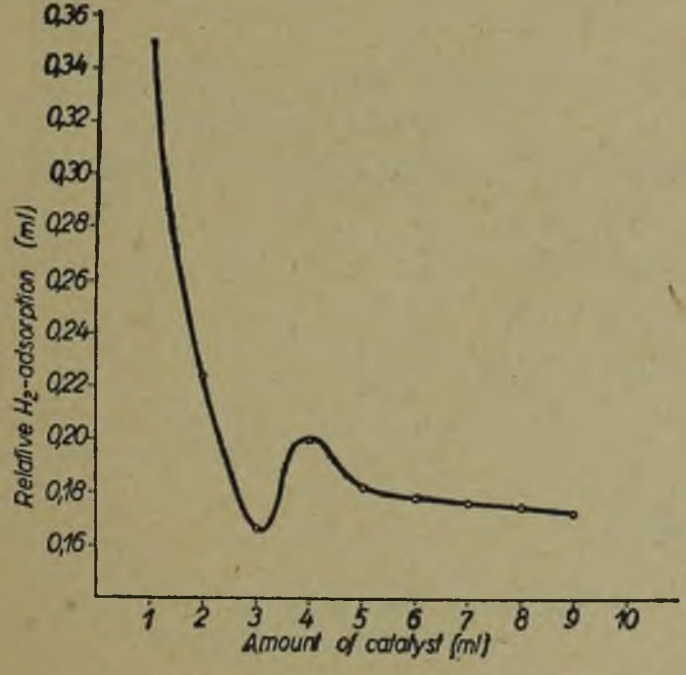
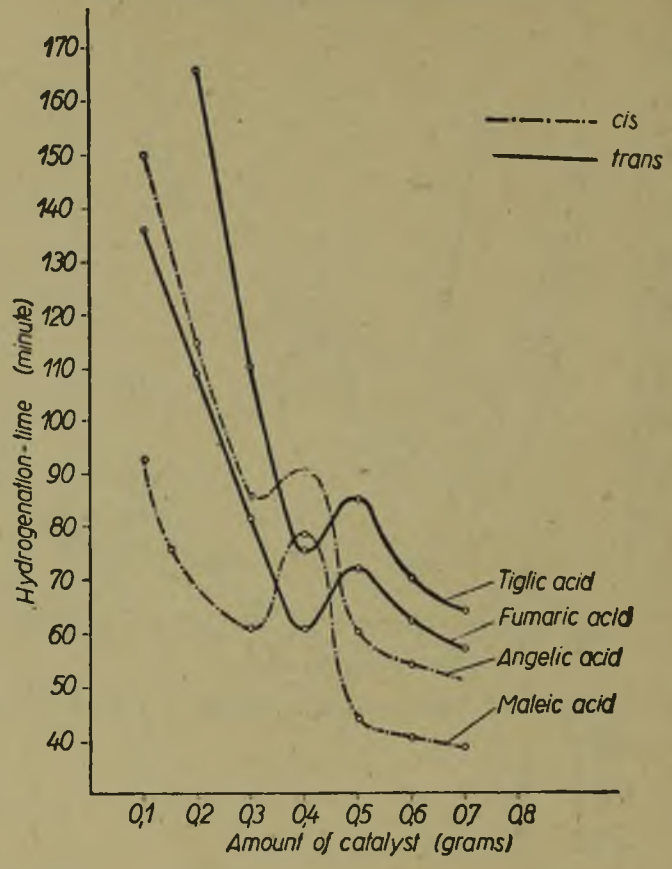


Figure V.

HYDROGENATION-TIME GRAPHS OF CIS-TRANS ISOMERS
with Pt catalyst on bone-black, marked "A".



H_2— ADSORPTION OF CATALYST as related ot 0,1 g of the catalyst.

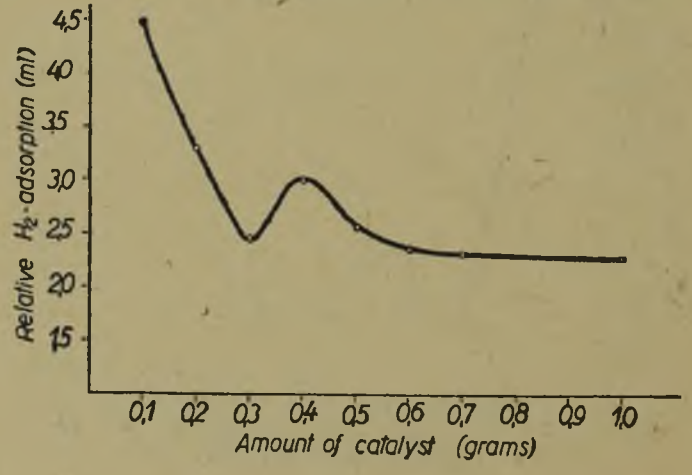
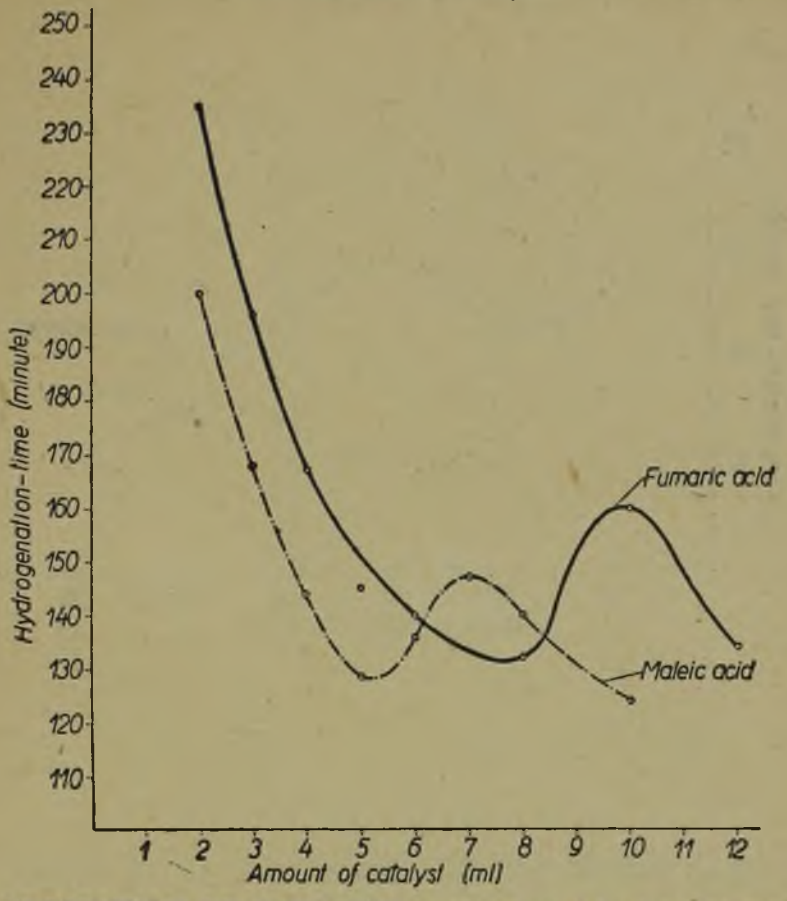


Figure VI.

HYDROGENATION-TIME GRAPHS OF MALEIC AND FUMARIC ACIDS
with colloidal Pt catalyst.



H_2-ADSORPTION OF CATALYST as related to 0,1 ml of the catalyst.

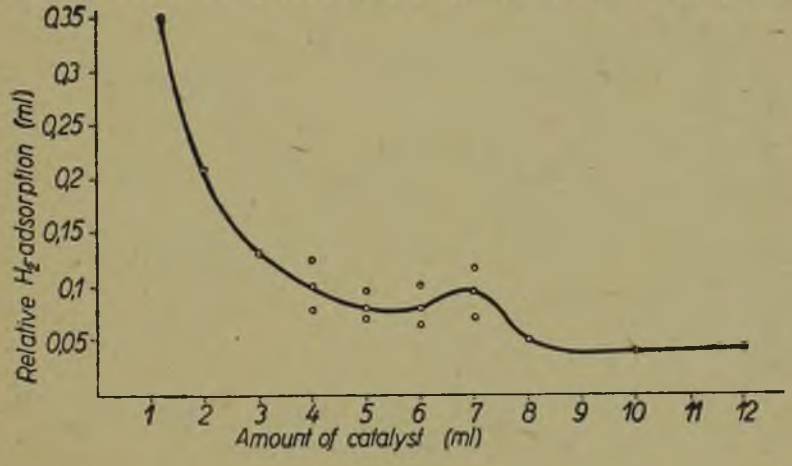
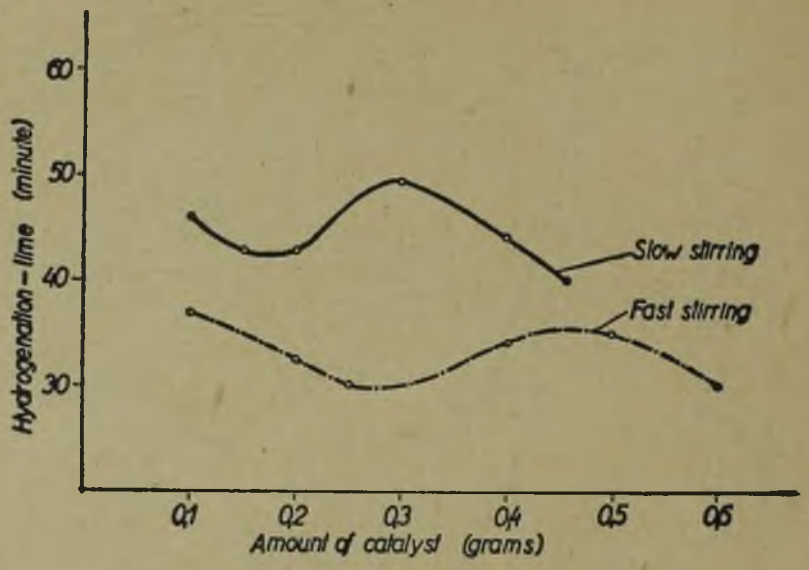


Figure VII.

HYDROGENATION-TIME GRAPHS OF CINNAMIC ACID
with Pd catalyst precipitated on bone-black, at fast and slow stirring.



RELATIVE H_2-ADSORPTION OF THE CATALYST at fast and slow stirring.

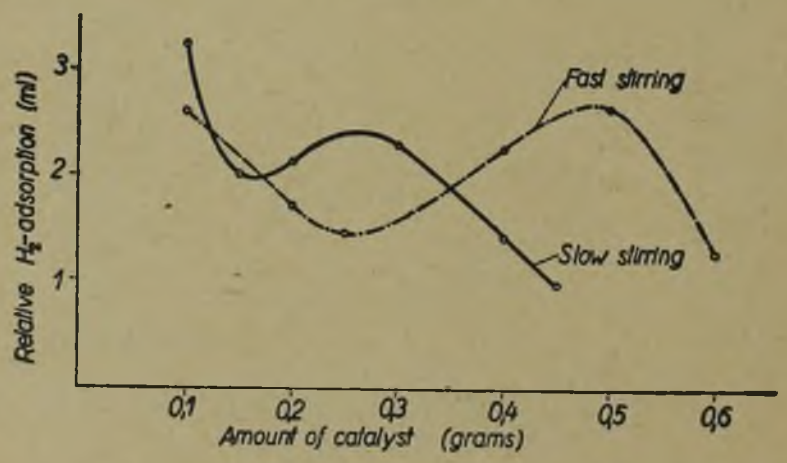
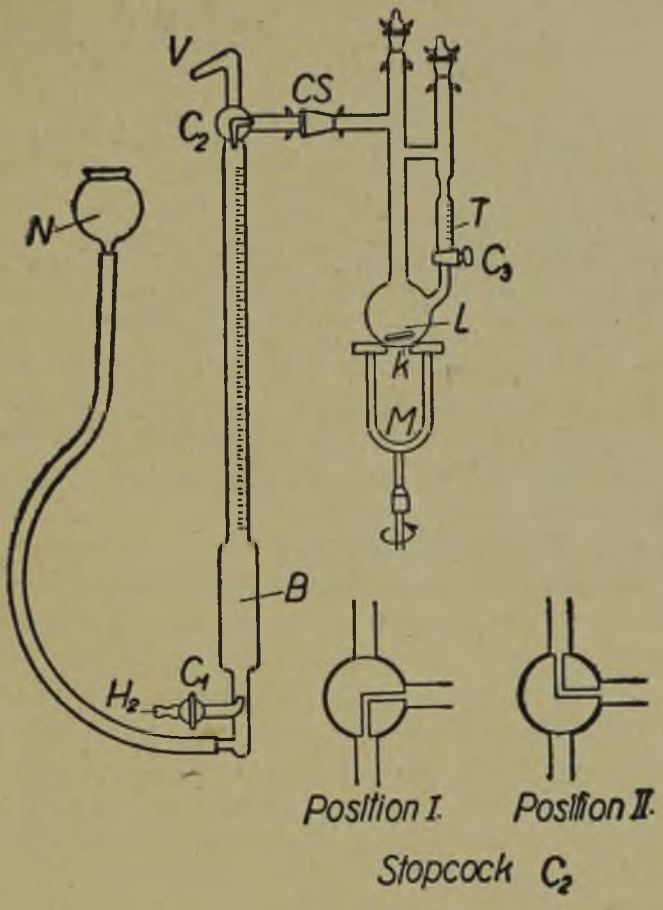


Figure VIII.

HYDROGENATION APPARATUS.



LITERATURE.

1. *S. Fokin*, Zeitschr. angew. Chem. *22*, 1492 (1909).
2. *C. Paal* and *A. Schwarz*, Ber. *48*, 994 (1915).
3. *I. F. Bogdanov* and *J. I. Baskirova*, Bull. Acad. Sci. URSS (Ser Chim.) *1936*. 91; C. *1937. I.* 2761.
4. *J. Salkind*, Journ. Russ. Phys. Chem. Ges. *46*, 1527; C. *1915. II.* 690.
5. *A. Kailan* and *F. Hartel:* Monatsh. Chem. *70*, 329 (1937); C. *1938. I.* 49.
6. *Z. Csűrös, K. Zech* and *I. Géczy*, Hungarica Acta Chimica *1*, 1 (1946).
7. *Z. Csűrös, K. Zech* and *T. Pfliegel*, Hung. Acta Chim. *1*, 24 (1946).
8. *H. S. Taylor*, J. Amer. Chem. Soc. *53*, 578 (1931).
9. *A. Osawa*, Tohoku Imp. Univ. *14*, 43; C. *1926. I.* 577.
10. *E. B. Maxted*, J. Chem. Soc. (London) *117*, 1280 (1920).
11. *W. Ostwald*, Kolloid-Z. *43*, 249, 268 (1927).
12. *P. Mehl*, Kolloid-Z. *56*, 299 (1931).
13. *L. Wöhler* and *W. Wenzel*, Kolloid-Z. *53*, 273 (1930).
14. *T. P. Papkova—Kwitzel*, Kolloid-Z. *66*, 155 (1934).
15. *C. Paal, H. Schiedewitz* and *K. Rauscher*, Ber. *60*, 1221 (1927); *C. Paal* and *H. Schiedewitz*, Ber. *63*, 766 (1930); Ber. *64*, 1521 (1931).
16. *I. E. Muskat* and *B. Knapp*, Ber. *64*, 779 (1931).
17. *C. Paal* and *J. Gerum*, Ber. *41*, 2273 (1908).
18. *J. W. Kern, R. L. Shriner* and *R. Adams*, J. Amer. Chem. Soc. *47*, 1147 (1925).
19. *R. N. Pease* and *L. Stewart*, J. Amer. Chem. Soc. *47*, 1235 (1925).
20. *W. W. Russel* and *L. G. Ghering*, J. Amer. Chem. Soc. *57*, 2544 (1935).
21. *J. B. Matthews*, Nature *157*, 407 (1946).
22. *L. Gattermann* and *H. Wieland*, Die Praxis des org. Chemikers, Walter de Gruyter & Co., 1943 (Page 368).
23. *A. Skita*, Ber. *45*, 3579 (1912).
24. *H. Kaffer*, Ber. *57*, 1263 (1924).
25. *A. Skita* and *W. A. Meyer*, Ber. *45*, 3585 (1912).

INVESTIGATIONS ON CATALYSTS. IV.:[1] CATALYTIC HYDROGENATION OF COMPOUNDS CONTAINING CARBONYL GROUP.

BY ZOLTÁN CSŰRÖS AND ISTVÁN SELLŐ.
(ORG. CHEM. TECHNOLOGICAL INSTITUTE OF THE TECHNICAL UNIVERSITY, BUDAPEST.)
RECEIVED : 18, III. 1947.

It is known that the catalytic reduction of the *CO* group is decidedly more difficult than the saturation of the ethylene bond. *Skita* and *Meyer* (1) found that aromatic and heterocyclic compounds, as well as most aldehydes and ketones — as opposed to other aliphatic and alicyclic double bonds — could not be reduced by the earlier known catalysts. Colloidal platinum with its more active surface, in a medium of glacial acetic acid, assures at a suitable pressure the hydrogenation of these compounds and the velocity of the hydrogenation is also greater than with platinum black.

In our experiments we wanted first of all to be convinced of the difference, which exists in the hydrogenation of aliphatic and aromatic aldehydes and ketones and also of those provided with an aromatic ring and containing the *CO* group in a side chain.

For this purpose we first hydrogenated an aliphatic α, β-unsaturated ketone (2-methylhexen-(3)-on-(5)), then an aliphatic aldehyde (croton aldehyde), aromatic aldehyde (benzaldehyde), also an aldehyde containing an aromatic ring (phenyl acetaldehyde) and lastly an α, β-unsaturated ketone (benzal acetone). These hydrogenations were done with colloidal *Pd*, *Pd* on bone-black, or colloidal *Pt*. No significant difference could be observed in the activity of the catalysts used.

According to *Ott* and *Schröter* (2), in the case of colloidal catalysts the protective colloid retards the reaction. The colloidal catalyst, however, has a larger surface than that on the bone-black, which eliminates the retardation effect attributed to the protective colloid.

In our experiments we found in every case that the compounds which could not be hydrogenated with colloidal *Pd* were not reducible with *Pd* precipitated on bone-black either. But — in the case of substances,

[1] See:
I. *Z. Csűrös, K. Zech* and *I. Géczy*, Hungarica Acta Chimica *1*, 1 (1946).
II. *Z. Csűrös, K. Zech* and *T. Pfliegel*, Hung. Acta Chim. *1*, 24 (1946).
III. *Z. Csűrös* and *E. Gergely*, née *Popper*, Hung. Acta Chim. Vol. I. (No. 4-5) 1-26 (1949).

which may be hydrogenated — the velocity of the saturation was considerably greater with *Pd* precipitated on bone-black than with colloidal catalyst. The *Pd* on bone-black used (0,1 g) had the same amount of metal as 1,814 ml colloidal *Pd*, i. e. it contained 5,66 mg *Pd*.

We found that hydrogenating benzaldehyde and phenyl acetaldehyde by 5 ml colloidal *Pd* (15 mg *Pd*-content) and 0,3 g *Pd* on bone-black (16,98 mg *Pd*-content) under identical conditions, the velocity of the hydrogenation was decidedly greater in both cases using *Pd* on bone-black, though the *Pd* used was only with 12,4% more. Our observations oppose to *Ott* and *Schröter*'s (2) statements, that under like conditions about five times as much is necessary of *Pd* on bone-black than of colloidal catalyst.

According to *Ginsberg* and *Ivanov* (3), *Pt* is quite as effective catalyst as *Pd*, except that the velocity of its hydrogenation is less. When hydrogenating methyl hexenon and croton aldehyde we also found that the velocity was less in the case of colloidal *Pt* than in that of colloidal *Pd*.

The reduction of the compounds mentioned above was performed in case of the colloidal *Pd* in a water-alcoholic medium, using *Pd* on bone-black in alcohol and glacial acetic acid and using colloidal *Pt* in acetic acid. The circumstances of the experiments were exactly identical. The temperature was between 20—23° C, the pressure about atmospheric. If it was not exactly 760 Hgmm, but it had the same value in all experiments, as the levelling bottle was kept at the same height. The total volumes were also constant and the velocity of stirring was the same during the experiments. The stirring was intensive resulting in a rapid diffusion, so that it was not necessarily the part of the process, which determined the rate of catalytic hydrogenation. Throughout our experiments we found, that the reduction, except for about the last 5—10% of the H_2 absorbed, occured according to a zeroth order.

In all experiments we used 0,001 mol of the substratum to be hydrogenated.

The results of the experiments are assembled in the Experimental Part in Tables and Graphs. There are shown the half-time of hydrogenation, the total H_2 absorbed, as well as the amount of H_2 consumed during stirring per unit mass of catalyst for the saturation, as function of the amount of catalyst used. It may be seen on these graphs, that the hydrogenation-time curve — in agreement with the experimental results of *Csűrös* and *Zech* with *Géczy* and *Pfliegel* respectively (4, 5) — pass through a local minimum and maximum corresponding to the local maximum and minimum of the velocity curves. The velocities given in the Tables are always calculated from half of the hydrogenating times, as the results can thus

better be compared. Namely the hydrogen-absorption occurs always according to zeroth order in the first half-time.

Methyl-hexenon was first hydrogenated by colloidal *Pd* in water—alcoholic medium. Depending on the amount of catalyst, the H_2 consumed varied between 16,62—29,61 ml. (Table Ia, Graph I, Figure b). Hydrogenating by a very small amount of catalyst and by that quantity at which the maximum of the curve is, as little hydrogen was consumed (16,62 or 16,83 ml) as, at the conditions given (1 atm and room temperature) corresponds only to 2/3 mol. Analysing the hydrogenated products it was observed that the $C = C$ bond was almost completely saturated, so in the case of consumption of 2/3 mol H_2 too.

According to *Weidlich* and *Meyer-Delius* (6) if unsaturated ketones are hydrogenated slowly enough, hydrodimerisation can occur. Sometimes this is the principal reaction. In certain conditions such dimeric products precipitate on the catalyst and so it loses its further effectiveness. The velocity of the reaction is just as important to the end products of the hydrogenation as to the reaction capacity of the intermediate products. The two *H* atoms do not enter the unsaturated molecule simultaneously, but one after the other. If the radicals are saturated among themselves more rapidly and easily than by the two *H* atoms, then hydrodimerisation occurs.

At the hydrogenation of methyl hexenon the $C = C$ bond was completely saturated, even if the H_2 consumption is less then 1 mol, that is the formation of dimeric products is probable. The extent of hydrodimerisation taking place as side reaction is probably the smaller, the greater is the rate of hydrogenation.

With colloidal *Pt* in glacial acetic acid the velocity of the hydrogenation was likewise slight, while the H_2 consumption was scarcely more than half a mol. With a greater amount of catalyst — consequently hydrogenating more rapidly — in case of colloidal *Pd* there was a consumption of more than 1 mol H_2.

Methyl hexenon, in the presence of *Pd* on bone-black, in alcohol and glacial acetic acid could also be hydrogenated as if only its double bond would have been able to react. Therefore we also carried out the hydrogenation by colloidal *Pt* and *Pd* precipiteted on bone-black in acetic acid or glacial acetic acid, for, according to *Packendorff* (7), in acidic medium the *Pt* catalyst is more active, while *Skita* (8) considers colloidal *Pt*, in glacial acetic acid also suitable for hydrogenation of aldehydes and ketones. *Skita* did these hydrogenations at 1 atm pressure gauge.

We found in all cases that at ordinary pressure with the above catalysts, at the conditions stated earlier, the aliphatic ketone group could

not be hydrogenated; at most there was some possibility of perhydrogenation in the unsaturated ketone after complete saturation of the double bond.

According to *Weidlich* and *Meyer-Delius* (6), in hydrogenating α, β-unsaturated ketones perhydrogenation usually occurs as an undesirable reaction. The double bond and with it also the *CO* group reduces without a decrease in the velocity of the hydrogenation after the absorption of 1 mol H_2. If we stop the hydrogenation after the absorption of 1 mol H_2, the product obtained contains, besides a large quantity of unsaturated ketone, saturated ketone and saturated hydrocarbon. It is typical of this sort of perhydrogenation processes that the absorption of H_2 can practically stop without all the starting material being reduced to hydrocarbon. The product then formed is a mixture of hydrocarbon and saturated ketone. It depends on the structure of the starting material and the catalyst, in what proportion the two components form.

Strauss (9) describes similar perhydrogenation, using benzal acetone and dibenzal acetone. In hydrogenating these the excess of the consumption of H_2 is about 1/5th mol, in the case of ketones containing the methoxyl group it is between 5/10 and 7/10ths mol.

Csűrös, Zech and *Géczy* (5) hydrogenated aliphatic unsaturated ketone (methyl heptenon) and unsaturated ketone connecting the *CO* group in a side chain to an aromatic ring (benzal acetone) with colloidal *Pd*, in alcoholic medium, in the presence of $FeSO_4$ and $Zn\ (OOC.CH_3)_2$. After absorption of 1 mol H_2 unsaturated alcohol was obtained in both cases; the double bond remained unaffected. According to *Adams* (10, 11, 12), Fe^{++} accelerates reduction of the *CO* group, while Zn^{++} inhibits the saturation of the double bond. Fe^{++} increases the stability of carbinol, so hindering its further reduction and assists the reduction of carbonyl to carbinol.

But according to *Csűrös, Zech* and *Pfliegel* (4), the *CO* group of unsaturated aliphatic aldehydes cannot be hydrogenated by *Pd*, either in acidic or alkaline medium, nor in the presence of Fe^{++} promoter. We now achieved entirely similar results using *Pd* on bone-black and colloidal *Pt* catalysts. Greater H_2 consumption than 1 mol was not observed either in alcoholic, or glacial acetic acidic medium or at adding Fe^{++}. Aromatic aldehyde, also in accordance with *Strauss* (9) could be reduced easily with colloidal *Pd* in water-alcoholic medium and with *Pd* precipitated on bone-black in alcohol.

Strauss and *Grindel* (9) hydrogenated compounds containing *CO* group in acetonic medium with colloidal *Pd* at 1 atm pressure and room temperature. As a result of these investigations they set up the theory that only

those ketones and alcohols can be hydrogenated to hydrocarbons, in the circumstances given above, in which the carbonyl or carbinol group is in α-position to the aromatic ring.

Skita (8) achieved with colloidal catalyst containing 0,08 g *Pt*, that 0,047 mol (5 grams) benzaldehyde absorbed 1 mol of H_2 in 5 hours at 1 atm pressure gauge. This was 1 hour in the case of a catalyst containing 0,24 g *Pt*. We suceeded in hydrogenating 0,001 mol (0,1065 g) benzaldehyde with 5 ml of colloidal *Pd* (0,015 g *Pd* content) in 71 minutes and with 0,3 g *Pd* on bone-black (0,017 g *Pd*) in 42.5 minutes, without pressure gauge.

The *CO* group of α, β-unsaturated ketone, connecting in a side chain to an aromatic ring (benzal acetone), could not be hydrogenated either with *Pd* on bone-black (in alcohol or glacial acetic acid) or with colloidal *Pt* (in acetic acid). The hydrogenation was finished after absorption of 1 mol hydrogen.

As opposed to this, saturated aldehyde connecting in a side chain to an aromatic ring (phenyl acetaldehyde) could be hydrogenated at a fairly good velocity by colloidal *Pd* in aqueous alcoholic and with *Pd* on bone-black in alcoholic medium. According to *Skita* and *Ritter* (13), this compound did not absorb H_2 by *Pd* even at 1 atm pressure gauge, and could be hydrogenated only on increasing the pressure to 5 atm. With colloidal *Pt* — at 1 atm pressure gauge — the reduction took 4 hours. In our experiments with *Pd* on bone-black, in alcoholic medium, the time of hydrogenation varied between 19 and 40,5 minutes (Table III), depending on the amount of catalyst, without pressure gauge.

On this basis it can be concluded from these experimental examples that with the above catalysts, in the circumstances given (i. e. without using pressure gauge) the *CO* group of aliphatic aldehydes and ketones cannot be reduced; while that of the aromatics can be, easily. The aldehyde group connecting in a side chain to the aromatic ring may be hydrogenated, but the ketone might be not. Therefore the phenyl radical promotes reducibility of the *CO* group to a greater degree in the aldehydes than in the ketones.

We also wanted to investigate how the substitution of different positions affected the velocity of hydrogenation of the *CO* group connected directly to the benzene ring. Only scattered literary data are to be found concerning the effect of substitutions.

According to *Strauss* (9) the *p*-methoxyl group accelerates the transformation of carbinol. He could not demonstrate this effect on the ethylene bond nor on the carbonyl group.

Bargellini and *Finkelstein* (14) found that the inhibitory effect of free phenolic *OH* was so great that the reduction of chalcons, in the case of more than one free *OH*, succeeded only with difficulty, and that of hesperetin, for example, could not be completed at all.

According to *Boskovitz* (15), in the case of benzal acetone a substituent in para position promotes the saturation of the $C = C$ bond, with the growth of the substituent the time of the absorption of the first mol of H_2 also diminishes. On the contrary, the *CO* group could not by hydrogenated either in *p*-oxy benzal acetone, nor in *p*-methoxy benzal acetone, but only in derivatives replaced by larger substituents, for example by tetra-acetyl glucose, but then too the absorption time of the second mol of H_2 was decidedly slower than of the first.

We hydrogenated benzaldehyde and *o*-, *m*- and *p*-oxy benzaldehyde with *Pd* on bone-black, in alcoholic medium, in a total volume of 15 ml, at 1 atm pressure and room temperature. As *Popper* (16) succeeded in extending *Csűrös, Zech* and *Géczy*'s (5) hydrogenation velocity curve to *Pd* on bone-black, we carried out the above hydrogenations with *Pd* on bone-black too. In each case — depending on the amount of the catalyst — the curve passed through a local maximum and minimum. According to Graph II. the maxima of the hydrogenation time curves are nearly at the same amount of catalyst, while the local minima vary with the amount of catalyst between 0,12—0,18 g, i. e., there is a very small interval between them. At the substituted derivatives the percentual differences between maximum and minimum are greater than at benazldehyde itself. The maximum value is gradually greater in the *m*-, *o*- and *p*-oxy benzaldehydes than in benzaldehyde itself; while the minimum value is gradually smaller in the *o*-, *p*- and *m*-oxy derivatives. The percentual difference between maximum and minimum is the greatest in the derivative substituted in the para position.

The literary data are contradictory as to whether substitution exerts an increasing or restraining effect on the velocity of hydrogenation. From our experimental results it can be concluded that the substitution not only increases the velocity of hydrogenation, but the maximum of the velocity curve grows, the minimum decreases; that is the percentual difference between the two extreme values is greater. It therefore depends on the quantity of catalyst chosen, which of the four substrata can be hydrogenated more rapidly.

We further took under investigation how different organic solvents affect the velocity of hydrogenation and how their effect are exerted. Literature on the influence of solvents on catalytic hydrogenation, in the

first place on the velocity of hydrogenation differs very much. The data are often completely contradictory.

Fokin (17) has already found that hydrogenations which did not succeed in acetonic medium could be carried out easily in alcoholic medium. *Paal* (18) hydrogenated unsaturated esters with *Ni*-powder containing *Pd*, in different solvents and concluded that certain solvents retarded hydrogenation, while others did not affect it. Benzene, for example, made the catalyst permanently ineffective. He failed to reactivate the catalyst by putting it into ether, then into hydrogen atmosphere or glowing it slightly in hydrogen. Acetone also had an inhibitory effect, ether and alcohol, on the contrary, did not make it passive. The behaviour of benzene and acetone, and of ether and alcohol respectively, can be explained as being that in the first named solvents the catalyst tends rather to adsorb the solvent than the H_2, while the H_2 pushes out the ether or alcohol adsorbed by the catalyst.

Bargellini and *Finkelstein* (14) observed that the rate of reaction depends on the solvent and benzene, as well as acetone, inactivated the catalyst. *Straus* and *Grindel* (9) on the contrary did not find acetone to have an inactivating effect.

According to *Adkins*, *Diwoky* and *Broderick* (19) the solvents affect not only the velocity of hydrogenation but also — when mixtures are hydrogenated — the distribution of hydrogen among the components. *Adkins* supposed, that the effect of the solvent on changing the velocity and selectivity was exerted through its important rôle in the formation and in the degree of stabilisation of intermediate products which have been created from the catalyst, H_2, substratum and the solvent.

According to *Bogdanov* and *Baskirova* (20) the solvent exerts an effect only on the rate of the reaction, without affecting the selectivity of the catalyst. Thus *Adkins'* (19) hypothesis, that the solvent affects not only the rate of the reaction but also the selectivity of the catalyst, cannot be applied to all cases.

To set the question in proper light we hydrogenated phenyl acetaldehyde in water, alcohol, glacial acetic acid and acetone, always in a total volume of 15 ml, with *Pd* on bone-black, varying the amount of the catalyst. *Csűrös* and *Popper* (16) had already proved that the curve of the quantity of H_2 absorbed — during stirring — per unit mass of catalyst runs similarly to the hydrogenation time curve. We therefore measured in different solvents and during stirring the amount of H_2 absorbed per unit mass of catalyst.

We used *Pd* on bone-black, as it adsorbs decidedly more H_2 than the colloidal catalyst does. The amount adsorbed could thus easily be

measured and compared. Figure *b* of Graph III shows the amount of H_2 adsorbed during stirring in different solvents (water, glacial acetic acid, alcohol, acetone) per 0,1 g of the catalyst. Saturation of the catalyst always took place in the same volume of solvent, i. e. 10 ml. 0,001 mol of the substance to be hydrogenated was dissolved in 5 ml of the solvent and added in every experiment to the catalyst already saturated.

According to Figures *a* and *b* of Graph III the half-time hydrogenation curves in all cases progress identically with the corresponding saturation curves, as the extreme values of the time curve and those of the saturation curve are at the same quantity of catalyst. The velocity of hydrogenation of phenyl acetaldehyde is the greatest in acetone, less in alcohol, more less in glacial acetic acid and the slowest in water. Comparing the half-time curve of hydrogen absorption in glacial acetic acid and alcohol with the saturation curve of the catalyst, it may be seen that in the case of 0,3 g catalyst the same amount of H_2 are necessary to saturate the catalyst. The two hydrogenation half-time curves also approach each other best at this quantity, i. e. here is the minimum of the half-time curve of hydrogenation in glacial acetic acid and the maximum of the curve in case of alcoholic medium. *Csűrös* and *Popper* (16) had already demonstrated that if we increase the diffusion by stirring sufficiently so that it is not the rate controlling step in the heterogeneous catalytic reaction, then the H_2 adsorption of the catalyst will in the first place determine the rate of hydrogenation. If the amount of the H_2 adsorbed per unit mass of catalyst is plotted as a function of the amount of catalyst used, the curve obtained runs similarly to the hydrogenation time curve.

Acetone, opposed to the experiences of *Paal* (18), *Fokin* (17) and *Bargellini* and *Finkelstein* (14) does not inactivate the catalyst, but indeed, in accordance with the experiences of *Strauss* and *Grindel* (9), it is a very useful medium for hydrogenation with *Pd*. It was our experience that the velocity of hydrogenation of phenyl acetyldehyde was the greatest in acetone. According to literary data — in the case of *Pt* catalyst — the velocity of hydrogenation was greater in glacial acetic acid than in alcohol, while others have found it to be the same. Our observations show that — with *Pd* on bone-black — phenyl acetaldehyde may be hydrogenated more rapidly in alcohol than in glacial acetic acid.

It may be seen in Graph III that the solvent changes the H_2 adsorption of the catalyst and consequently affects the velocity of hydrogenation. The lyosorption of the different solvents are of different extent on the same adsorbent. The solvent, due to lyosorption alters the heterogeneous surface of the catalyst, thereby determining the amount of H_2 necessary for its saturation, that is, the velocity of hydrogenation will be a functio alson

of the lyosorption of the solvent. Using the same catalyst a relationship may exist between a physical constant of the solvent and the rate of hydrogenation. The physical constant of the solvent determines the value of the lyosorption, thus having an important rôle in developing the catalyst's surface and is consequently a decisive factor of the velocity of hydrogenation.

According to *Ostwald* and *Haller* (21) lyosorption changes contrarywise to the dielectric constant. If, instead of the dielectric constant we compare the specific polarisation with the lyosorption, we get a better result. Given that $P = \frac{E-1}{E+2} \cdot \frac{1}{d}$ (P = specific polarisation; E = dielectric constant; d = density), it is apparent from the formula that the specific polarisation also depends on the density. The greater is the thickness of the lyosphere, the smaller the dielectric constant or the specific polarisation. The specific polarisation of the solvent is probably one of the physical constants which affect the velocity of hydrogenation.

Among the solvents used acetone had the smallest viscosity. The stirring, therefore — though under identical working conditions — was the most rapid in acetone and so it is possible that this played a rôle in it that the phenyl acetaldehyde could be hydrogenated more rapidly in acetone than in other, more viscous solvents.

On this basis it can be concluded that the medium has undoubtedly a decisive effect on the velocity of catalytic hydrogenation, though according to *Ginsberg* and *Ivanov* (3) the medium is of minor importance if the substance to be hydrogenated is dissolved in it. The solvent affects the velocity of hydrogenation by altering the surface of the catalyst through lysorption and thereby determines the amount of H_2 necessary to saturate the catalyst.

SUMMARY.

Investigations were made in the first place on hydrogenation of aliphatic and aromatic aldehydes and ketones, as well as those linking in a side chain to an aromatic ring. We hydrogenated for this purpose methyl hexenon, croton aldehyde, benzaldehyde, benzal acetone and phenyl acetaldehyde. The experiments were carried out with colloidal *Pd* and with *Pd* on bone-black, as well as with colloidal *Pt*. We found that at the experimental conditions (ordinary pressure and room temperature) the *CO* group of aliphatic aldehydes and ketones could be hydrogenated by the above catalysts neither in alcohol nor in glacial acetic acid. According to *Csűrös, Zech* and *Géczy* (5) the *CO* group of aliphatic ketones can be reduced by colloidal *Pd* in aqueous alcoholic medium, using Fe^{++} and Zn^{++}

promoters. Reduction of the *CO* group of aliphatic aldehydes, at similar conditions, cannot be achieved even in glacial acetic acid. In hydrogenation of α, β-unsaturated ketones with colloidal catalysts it is probable that dimeric products are also formed. The less the velocity of hydrogenation is, the greater is their amount.

The aldehydes linked to an aromatic ring in a side chain, unlike the ketones, can be easily hydrogenated. The phenyl radical, therefore, promotes the reduction of the aldehydes to a greater extent than that of the ketones. We were also successful in hydrogenating phenyl acetaldehyde with colloidal *Pd* and *Pd* on bone-black without pressure gauge. According to *Skita* and *Ritter* (13) phenyl acetaldehyde, with colloidal *Pd*, at 1 atm pressure gauge absorbed no trace of H_2 and could be hydrogenated only at 5 atm pressure.

We found that, though the hydrogenation velocity was greater with *Pd* on bone-black than with colloidal *Pd*, the compounds which could not be saturated with colloidal *Pd* could not be hydrogenated with *Pd* precipitated on bone-black either.

We investigated the effect of substitution in the ortho-, meta- and para-positions on the rate of hydrogenation of the *CO* group attached directly to the benzene ring. For this purpose we hydrogenated benzaldehyde and *o*-, *p*- and *m*-oxy benzaldehyde in the presence of varying quantities of *Pd* on bone-black. Substitution in para position made the greatest change in the velocity of hydrogenation, that of the meta position the smallest. The substituents increase the percentual difference between the local maximum and minimum of the velocity curve; i. e., with different quantities of catalyst they affect the velocity of hydrogenation differently.

The medium necessarily affects the rate of catalytic hydrogenation. We hydrogenated phenyl acetaldehyde with varying amounts of *Pd* on bone-black in water, alcohol, glacial acetic acid and acetone and found, in agreement with *Strauss* and *Grindel* (9) and on the contrary to *Paal* (18), *Fokin* (17) and *Bargellini* and *Finkelstein* (14), that the acetone does not inactivate the *Pd* catalyst, but indeed of all the solvents used the velocity of hydrogenation was the greatest in acetone.

In the solvents tested (water, alcohol, glacial acetic acid, acetone) — in agreement of the experiences of *Csűrös* and *Zech* with *Géczy*, as well as with *Pfliegel* (5, 4) — the hydrogenation time curves taken as function of the quantity of catalyst all pass through a local maximum and minimum. These curves shift compared to each other. Therefore the solvent affects at the most the position of the curve and the extent of the velocity of hydrogenation, but not the minimum-maximum character. Extending

the maximum-minimum rule to various solvents, we succeeded in proving the more general validity of this rule.

We confirmed the observation of *Csűrös* and *Popper* (16), that the curve of the quantity of H_2 necessary to saturate the catalyst, taken as function of the amount of catalyst, runs similarly to the hydrogenation time curve. The solvent affects the velocity of hydrogenation by changing the surface of the catalyst through lyosorption, thus influencing the catalyst's H_2 adsorption.

EXPERIMENTAL PART.

Apparatus.

All the experiments were carried out in the semi-micro hydrogenating apparatus employed by *Csűrös, Zech* and *Géczy* (5), as modified by *Csűrös, Zech* and *Pfliegel* (4), with *Weygand* and *Werner*'s (23) magnetic stirrer.

Preparation of the catalysts.

Colloidal *Pd* was prepared according to *Skita* (24). *Pd* content of the colloidal solution was 0,3003 g *Pd*/100 ml, or 0,003 mg *Pd*/ml. *Pd* on bone-black was prepared according to *Gattermann* and *Wieland* (25). *Pd* content of the catalyst: 5,66 mg *Pd*/0,1 g catalyst. Hence 1,884 ml colloidal *Pd* is of equal value in metal content to 0,1 g *Pd* on bone-black, or 1 ml colloidal *Pd* is equal to 0,053 g *Pd* on bone-black.

Colloidal *Pt* was prepared after *Skita* and *Meyer* (26). *Pt* content of the colloidal catalyst: 0,2048 g *Pt*/100 ml, i. e. 2,048 mg *Pt*/ml.

Preparation of the $FeSO_4$ promoter solution: 0,06 g $FeSO_4 . 7 H_2O$ is dissolved in distilled water and filled up to 100 ml.

Double bond determinations.

Quantitative determination of the double bond was made by *M. C. Ilhiney*'s (22) bromine number determination.

Hydrogenations.

First series of experiments:

I. a. *2-methyl-hexen-(3)-on-(5)*:

$$(CH_3)_2 = CH - CH = CH - CO - CH_3.$$

0,2 mol alcoholic solution: 2,2417 g (0,02 mol) ketone was dissolved in alcohol and filled up to 100 ml. We hydrogenated 5 — 5 ml of the standard solution in a total volume of 20 ml.

1. We hydrogenated 5 ml of the above solution with colloidal *Pd*, in about a 50% aqueous alcoholic solution. At each time we added 5 ml 96% alcohol to the 5 ml standard solution and filled up the varying amounts of colloidal *Pd* with distilled water to 10 ml.

TABLE I/A.

Hydrogenation of methyl-hexenon with colloidal Pd, in aqueous alcoholic medium

Amount of catalyst in ml	H_2 consumed in ml	Hydrogenation time, in minute	Hydrogenation time to absorb 12 ml H_2	Rate of hydrogenation, ml/minute	$C = C$ bond saturation in %
0,5	16,62	138,0	95,0	0,126	97,3
1,0	23,01	68,0	30,0	0,400	99,2
2,0	24,18	55,0	18,5	0,649	96,8
4,0	22,89	58,1	29,0	0,414	98,7
6,0	21,01	75,0	40,0	0,300	99,1
8,0	16,83	99,3	48,0	0,250	99,0
10,0	29,61	65,2	16,5	0,727	98,7

2. 5 ml of 0,2-mol methyl hexenon solution was hydrogenated with 0,3 g *Pd* on bone-black in alcoholic medium. Velocity of hydrogenation: 0,364 ml H_2/min.

3. 5 ml of 0,2-mol methyl hexenon solution was hydrogenated with 0,3 g *Pd* on bone-black, in glacial acetic acid. Velocity of hyrogenation: 0,341 ml H_2/min.

4. 5 ml solution, 5 ml colloidal *Pt*, in glacial acetic acid. Velocity: 0,153 ml H_2/min.

I. b. *Hydrogenation of croton aldehyde.*

$$(CH_3 - CH = CH - CHO).$$

0,2-mol croton aldehyde solution: 1,4009 (0,02 mol) croton aldehyde was dissolved in 96% alcohol and filled up to 100 ml. 5 ml of this staff solution (0,001 mol aldehyde) was hydrogenated in a total volume of 20 ml.

1. 5 ml solution, 0,3 g *Pd* on bone-black, alcoholic medium. Velocity of hydrogenation: 0,566 ml H_2/min.

2. 5 ml solution, 0,3 g *Pd* on bone-black, in glacial acetic acid; 0,476 ml H_2/min.

3. 5 ml solution, 0,3 g *Pd* on bone-black, glacial acetic acid, 1,0 ml $FeSO_4$ solution added. Rate of hydrogenation: 0,410 ml H_2/min.

4. 5 ml solution, 5 ml colloidal *Pt*, glacial acetic acid, 1 ml $FeSO_4$ solution added. Rate of hydrogenation: 0,177 ml H_2/min.

I. c. *Hydrogenation of benzal acetone*

$$(C_6H_5 - CH = CH - CO - CH_3).$$

0,2-mol alcoholic benzal acetone solution: 2,9216 g (0,02 mol) ketone is dissolved in 96% alcohol and filled up to 100 ml. 5 ml of this is hydrogenated in a total volume of 20 ml.

1. 5 ml solution, 5 ml colloidal *Pd*, aqueous alcoholic medium. Rate of hydrogenation: 0,352 ml H_2/min.

2. 5 ml solution, 0,3 g *Pd* on bone-black, alcoholic medium; 0,759 ml H_2/min.

3. 5 ml solution, 0,3 g *Pd* on bone-black, glacial acetic acid; 0,741 ml H_2/min.

4. 5 ml solution, 5 ml colloidal *Pt*, glacial acetic acid; 0,343 ml H_2/min.

I. d. *Hydrogenation of benzaldehyde.*

0,2-mol alcoholic solution: 2,121 g (0,02 mol) benzaldehyde is dissolved in 96% alcohol and filled up to 100 ml. 5 ml contains 0,001 mol benzaldehyde. Total volume 20 ml.

1. 5 ml solution, 5 ml colloidal *Pd*, aqueous-alcoholic medium; rate of hydrogenation: 0,354 ml H_2/min.

2. 5 ml solution, 0,3 g *Pd* on bone-black, alcoholic medium; 0,645 ml H_2/min.

I. e. *Hydrogenation of phenyl acetaldehyde.*

2,4013 g (0,02 mol) aldehyde is dissolved in 96% alcohol and filled up to 100 ml. 5 ml of this contains 0,001 mol aldehyde. Reduction was made in a total volume of 20 ml.

1. 5 ml solution, 5 ml colloidal *Pd*, aqueous alcoholic medium; 0,423 ml H_2/min.

2. 5 ml solution, 0,3 g *Pd* on bone-black, alcoholic medium; 0,923 ml H_2/min.

Second series of experiments.

Hydrogenation of benzaldehyde and of o-, m- and p-oxy benzaldehyde.

0,2-mol alcoholic benzaldehyde solution, prepared as in I. d., was used for these experiments. The 0,2-mol alcoholic solutions of *o-*, *m-* and *p*-oxy benzaldehyde were made by dissolving 2,441 g (0,02 mol) aldehyde in 96% alcohol and filling it up to 100 ml. 5 ml of each of the above solutions were hydrogenated always, in a total volume of 15 ml, in the presence of varying amounts of *Pd* on bone-black. 5 ml of the above solution was added to the *Pd* catalyst suspended in 10 ml of 96% alcohol.

TABLE II.

Hydrogenation of benzaldehyde and of o-, m- and p-oxy benzaldehyde with Pd on bone-black in alcoholic medium.

	Time of hydrogenation, in minutes, to absorb 24 ml H_2:					
benzaldehyde	43,5	34,6	37,5	38,2	27,8	27,0
o-oxy benzaldehyde	41,9	38,4	29,3	48,0	27,4	27,2
m-oxy benzaldehyde	39,8	36,0	26,9	39,5	35,7	32,2
p-oxy benzaldehyde	37,5	29,8	39,0	50,1	27,4	26,8
Amount of catalyst	0,05	0,1	0,2	0,3	0,4	0,5 g
	Time of hydrogenation, in minutes, to absorb 12 ml H_2:					
benzaldehyde	19,7	15,5	17,1	17,3	12,7	12,4
o-oxy benzaldehyde	19,6	16,8	13,2	22,3	12,5	12,4
m-oxy benzaldehyde	18,9	15,9	12,4	18,2	16,3	14,7
p-oxy benzaldehyde	17,0	13,4	14,7	23,4	12,5	12,3
Amount of catalyst	0,05	0,1	0,2	0,3	0,4	0,5 g

	Rate of hydrogenation, ml H_2/minute:					
benzaldehyde	0,609	0,774	0,702	0,693	0,946	0,963
o-oxy benzaldehyde	0,612	0,726	0,909	0,538	0,950	0,963
m-oxy benzaldehyde	0,640	0,753	0,963	0,659	0,736	0,816
p-oxy benzaldehyde	0,706	0,895	0,816	0,513	0,950	0,975
Amount of catalyst	0,05	0,1	0,2	0,3	0,4	0,5 g

Third series of experiments:

Hydrogenation of phenyl acetaldehyde in different solvents.

We prepared 0,2-mol aqueous, alcoholic, glacial acetic acidic and acetonic solutions of phenyl acetaldehyde by dissolving 2,4013 g (0,02 mol) aldehyde in the above media and filling up the solution with the same solvent to 100 ml.

We hydrogenated 5 ml of the above solutions (0,001 mol aldehyde) in a total volume of 15 ml. In all the above solvents the *Pd* on bone-black was saturated with H_2 during stirring in a total volume of 10 ml. After adsorption of the H_2 we added 5 ml of the 0,2-mol solution to be hydrogenated.

TABLE III.

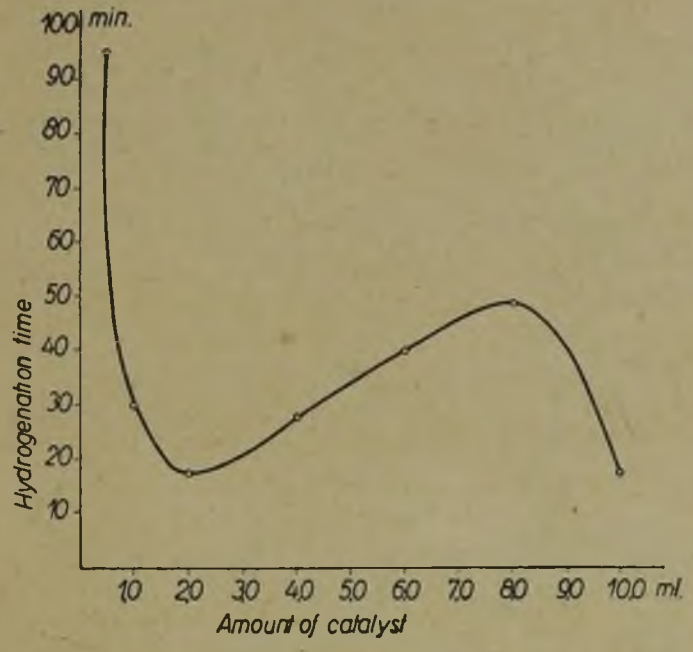
Hydrogenation of phenyl acetaldehyde in different solvents, with Pd on bone-black and H_2 adsorption of the catalyst.

Amount of catalyst, g	Total H_2 adsorption of catalyst, ml	H_2 adsorption per 0,1 g catalyst, ml	Hydrogenation-time, in min. to absorb		Rate of hydrogenation, ml/minute
			24 ml	12 ml	
			H_2		
Aqueous medium:					
0,1	3,52	3,52	192,3	87,5	0,137
0,2	4,10	2,05	146,0	67,0	0,179
0,3	8,42	2,81	183,1	82,0	0,146
0,4	9,23	2,31	146,5	66,5	0,180
0,5	10,05	2,01	103,0	48,5	0,247
Alcoholic medium:					
0,05	2,60	5,20	40,5	18,7	0,636
0,1	2,38	2,38	34,3	15,6	0,769
0,2	3,62	1,81	22,8	10,3	1,165
0,3	9,43	3,14	26,5	12,1	0,992
0,4	10,29	2,57	19,9	9,0	1,333
0,5	10,84	2,17	19,0	8,9	1,348
Glacial acetic acidic medium:					
0,1	15,58	15,58	71,1	32,1	0,374
0,2	22,20	11,10	45,6	20,8	0,577
0,3	9,92	3,31	31,6	14,2	0,845
0,4	22,93	5,73	34,6	15,9	0,755
0,5	13,25	2,65	31,5	13,7	0,876
Acetonic medium:					
0,1	1,30	1,30	25,6	11,9	1,008
0,2	4,44	2,22	12,3	5,4	2,222
0,3	6,90	2,30	13,5	5,8	2,069
0,4	7,04	1,76	10,4	4,5	2,666
0,5	8,06	1,61	7,6	3,1	3,871

Figure I.

2-METHYL-HEXEN-(3)-ON-(5) with colloidal Pd catalyst

a) *Hydrogenation half-time curve :*



b) *Complete H_2-absorption :*

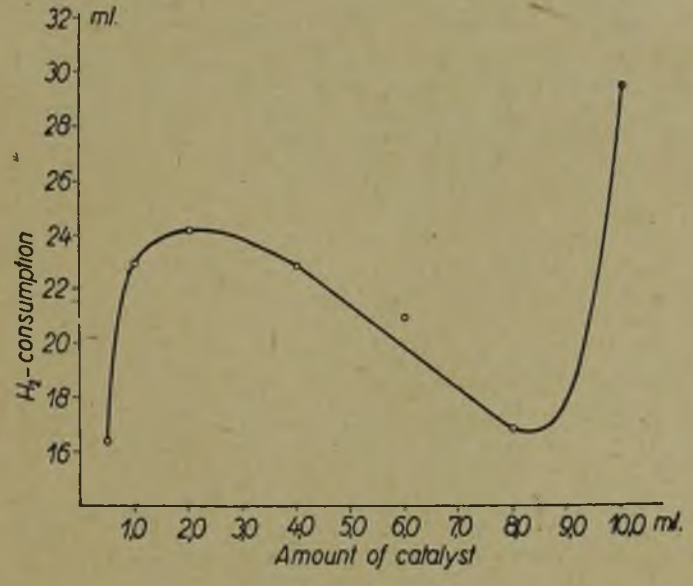


Figure II.

THE HYDROGENATION HALF-TIME CURVES OF BENZALDEHYDE AND o-, m- AND p-OXY-BENZALDEHYDE,
with Pd catalyst on bone black.

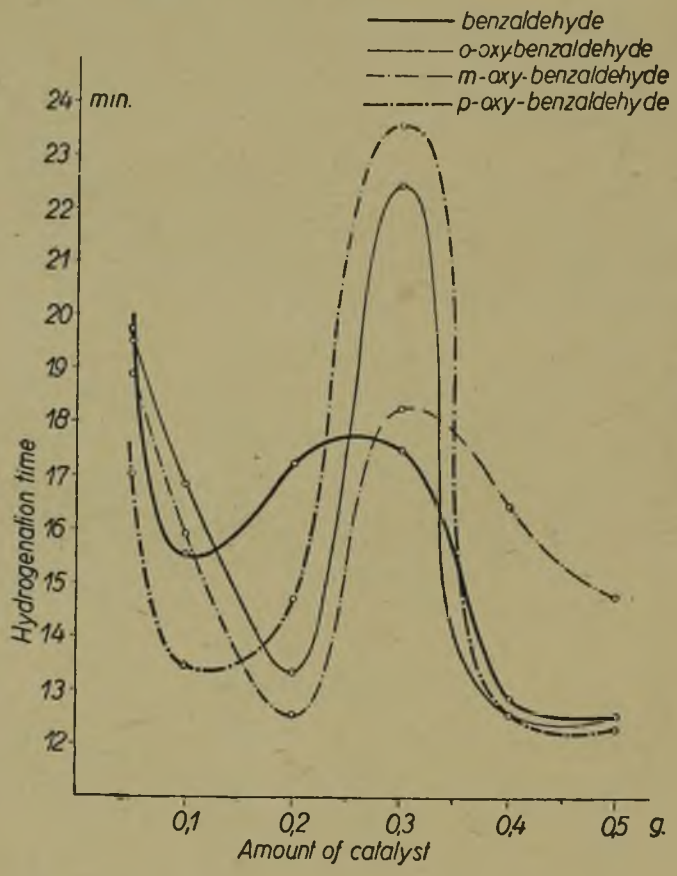
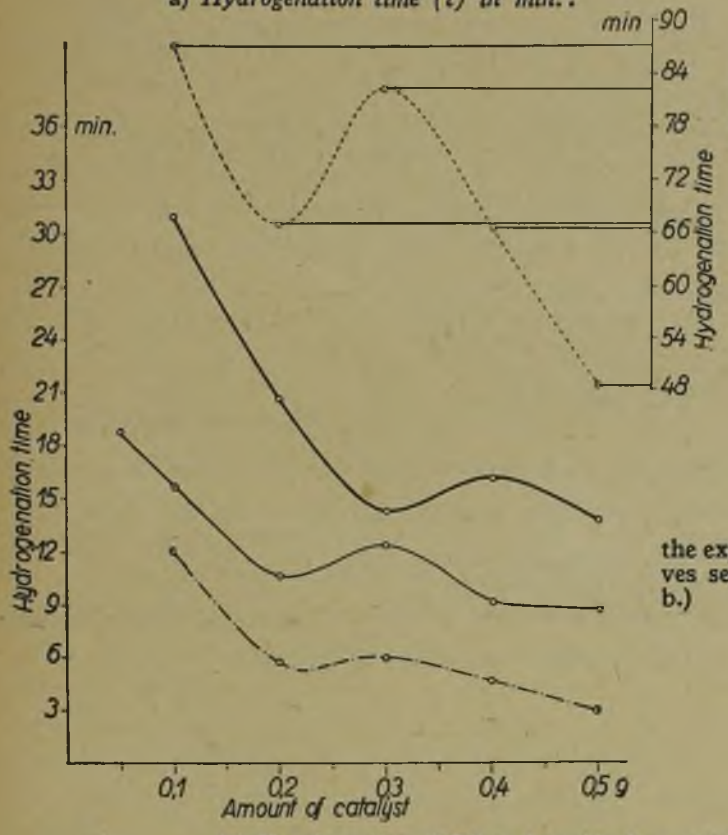


Figure III.

THE HYDROGENATION HALF-TIME CURVES OF PHENYL ACETALDEHYDE,
with Pd catalyst on bone black.

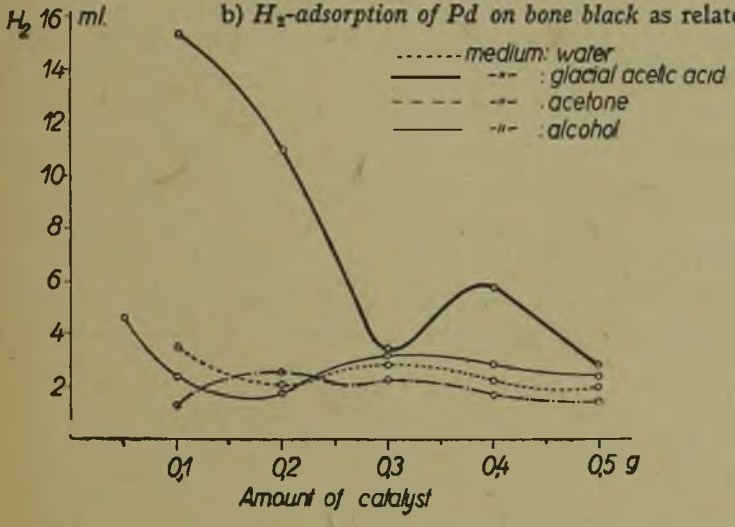
a) *Hydrogenation time (t) in min.:*



(The scale at the right relates to the curve taken in aqueous medium)

the explanation of the curves see below, at Figure b.)

b) *H_2-adsorption of Pd on bone black* as related to 0,1 g catalyst:



LITERATURE.

1. *A. Skita* and *W. A. Meyer*, Ber. *45*, 3590 (1912).
2. *E. Ott* and *B. Schröter*, Ber. 60, 624 (1927).
3. *A. S. Ginsberg* and *A. P. Ivanov*, Journ. Russ. Phys. chem. Ges. *62*, 1991 (1930); C. *1931. II.* 2416.
4. *Z. Csűrös, K. Zech* and *T. Pfliegel*, Hung. Acta Chim. *1*, 24 (1946).
5. *Z. Csűrös, K. Zech* and *I. Géczy*, Hung. Acta Chim. *1*, 1 (1946).
6. *H. A. Weidlich* and *M. Meyer—Delius*, Ber. *74*, 1195 (1941).
7. *K. Packendorff*, Ber. *67*, 905 (1934).
8. *A. Skita*, Ber. *48*, 1486 (1915).
9. *F. Strauss* and *H. Grindel*, Ann. *439*, 276 (1924).
10. *R. Adams* and *B. Carvey*, J. Am. Chem. Soc. *48*, 477 (1926).
11. *R. Adams* and *V. Tuley*, J. Am. Chem. Soc. *47*, 3061 (1925).
12. *R. Adams*, J. Am. Chem. Soc. *49*, 2101 (1927).
13. *A. Skita* and *H. Ritter*, Ber. *43*, 3393 (1910).
14. *G. Bargellini* and *M. Finkelstein*, Gazz. Chim. Ital. *42*, II. 417 (1912); C. *1913, I.* 294.
15. *L. Boskowitz*, Dissertation, Budapest (1944).
16. *Z. Csűrös* and *E Gergely*, née *Popper*, Hung. Acta Chim. Vol. *1.* (No. 4–5) 1-26 (1949); *E. Popper*, Dissertation, Budapest (1946).
17. *S. Fokin*, Journ. Russ. Phys. Chem. Ges. *39*, 607 (1907); C. *1907. II.* 1324.
18. *C. Paal*, Ber. *44*, 1013 (1911).
19. *H. Adkins, F. F. Diwoky* and *A. E. Broderick*, J. Am. Chem. Soc. *51*, (2) 3418 (1929).
20. *I. F. Bogdanov* and *J. I. Baskirova*, Bull. Acad. Sci. URSS., Ser. Chim. *1938.* Nr. 2, 529; C. *1940. II.* 1851.
21. *W. Ostwald* and *W. Haller*, Kolloid-Chem. Beih. *29*, 385 (1929).
22. *M. C. Ilhiney*, J. Am. Chem. Soc. *21*, 1087 (1899).
23. *C. Weygand* and *A. Werner*, J. Pract. Chem. *140*, 330 (1935).
24. *A. Skita*, Ber. 45, 3579 (1912).
25. *L. Gattermann* and *H. Wieland*, Die Praxis des organischen Chemikers. 1943. (Page 368).
26. *A. Skita* and *W. A. Meyer*, Ber. *45*, 3585 (1912).

INVESTIGATIONS ON CATALYSTS. V.:[1] HETEROGENEOUS CATALYTIC AUTOXIDATION OF BENZALDEHYDE.

BY ZOLTÁN CSŰRÖS, ISTVÁN GÉCZY AND ÁGNES LENGYEL, NÉE FARAGÓ.

(ORG. CHEM. TECHNOLOGICAL INSTITUTE OF THE TECHNICAL UNIVERSITY, BUDAPEST.)

RECEIVED : 21, VIII. 1947.

THEORETICAL PART.

A) *Introduction and Literature.*

In connection with catalytical autoxidation, a large number of investigations have been concerned chiefly with the inhibition of the process and not its promotion. Consequently the effect of the amount of catalyst on the velocity of autoxidation was investigated with regard to negative catalysis.

According to the results of *Moureu* and *Duffraise* (1), *Bäckström* (2) and *Milas* (3) resp., the velocity of autoxidation decreases in proportion to the increase of the anti-oxygen concentration. This phenomenon can be said to be of general validity, as it has been confirmed by most authors.

In respect to positive catalysis, however, far less informations may be found on the effects of the quantities of catalyst.

Berl and *Winnacker* (4) showed that the autoxidation velocity of benzaldehyde grew in direct proportion to the increasing amounts of metallic salt catalyst added. According to *Raymond* (5), the rate of this process increases proportionally to the concentration of the ions, i. e., to the square root of the amount of catalyst. In respect to heterogeneous catalysis *Brunner* (6) states that in the autoxidation of benzaldehyde the velocity of the process increases in almost direct proportion to the increase of the amount of pumice catalyst used.

This finding agrees superficially with the hypothesis which until not long ago was maintained in respect to other catalytic processes. Recently, however, *Csűrös, Zech* and *Géczy* (7), in connection with the heterogeneous

[1] See:
I. *Z. Csűrös, K. Zech* and *I. Géczy*, Hungarica Acta Chimica *1*, 1 (1946).
II. *Z. Csűrös, K. Zech* and *T. Pfliegel*, Hung. Acta Chim. *1*, 24 (1946).
III. *Z. Csűrös* and *E. Gergely* née *Popper*, Hung. Acta Chim. Vol. *1*. (No. 4-5) 1-26 (1949).
IV. *Z. Csűrös* and *I. Sellő*, Hung. Acta Chim. Vol. *1*. (No. 4-5) 27-44 (1949.)

catalysis of hydrogenations, observed the phenomenon, that the velocity of the catalytical process did not change linearly with changes in the amount of catalyst, but passed through a maximum and minimum. The same results were obtained by *Buzágh* and *Molnár* (8) dealing with the hetero-homogeneous catalysis of H_2O_2 decomposition as effect of varying amounts of adsorbent (silica gel).

On this basis, the aim of our investigations was to determine by studying the conditions of heterogeneous catalysis in autoxidation processes and the effect of the quantity of catalyst, whether the phenomenon mentioned above might exist in this case too.

We chose benzaldehyde as our model. Namely, *Raymond* (5) and *Brunner* (6) consider the autoxidation of benzaldehyde to be a type-reaction, phenomena observed in relation to it being applicable to the autoxidation of other aldehydes and a good many other substances too. It is also suitable, therefore, for carrying out experiments of this nature, for it is fairly easy to prepare in a pure state and disturbing side reactions, such as condensation and polymerisation do not occur during autoxidation *(Brunner)*.

Wöhler and *Liebig* (9), who first isolated benzaldehyde and produced it in a pure state, had already observed that, exposed to air, benzaldehyde was oxidised to benzoic acid and that sunlight greatly accelerated this transformation. *Schönbein* (10) confirmed this statement by exact experiments.

Bäckström (2) proved among other compounds on benzaldehyde his theory, that the mechanism of autoxidation processes occurs generally according to chain reactions both in light and darkness. *Engler* and *Wild* (11) established that the autoxidation of benzaldehyde is brought also through peroxides. Molecular oxygen additionates to the benzaldehyde molecules and, in their opinion, the intermediate peroxide thus formed is nothing else, but dibenzoyl-superoxyde: $(C_6H_5CO)_2O_2$. *Baeyer* and *Villiger* (12), however, consider the perbenzoic acid as intermediate product and have shown experimentally that synthetic perbenzoic acid with an equivalent amount of benzaldehyde changes in a few minutes to benzoic acid. In their opinion, therefore, the mechanism of the autoxidation of benzaldehyde takes place in two steps.

According to some authors the primary reaction product is not perbenzoic acid but some very labile "mol-oxide" *(Staudinger* (13)*)*, much richer in energy, which rapidly changes, possibly through another series of peroxides, into perbenzoic acid, with much less energy-content *(Almquist* and *Branch* (14)*)*. They were unable to isolate this labile "mol-oxide", however, and could only form theories as to its structure.

But this opinion does not change the essentials of the process; *Baeyer* and *Villiger*'s (12) ideas from the mechanism of benzaldehyde autoxidation has been accepted and confirmed by all later authors. The mechanism of the autoxidation of benzaldehyde can therefore be considered as elucidated. Opinion is still divided, however, as to the factors necessary to induce the process, i. e., the initial activation.

According to *Kühn* and *Meyer* (15), the autoxidation of benzaldehyde is caused by the catalytic effect of ions of heavy metals being always present as impurities. These two authors were successful in preparing completely pure benzaldehyde at liquid air temperature by fractionated crystallisation and this in the dark was not oxidised at all. In the opinion of other authors the autoxidation of benzaldehyde is a heterogeneous catalytic process and an adsorption catalysis is the cause of the initial activation.

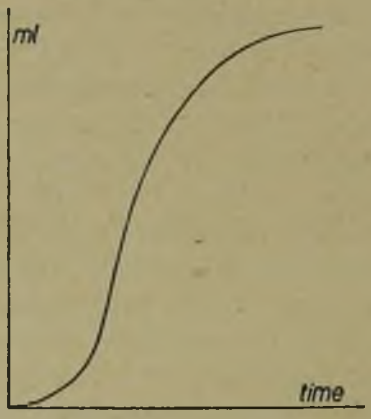
According to *Raymond*'s theory (5), completely pure, catalyst-free benzaldehyde will not be oxidised theoretically in the dark; the slight autoxidation observed always is caused by the catalysing effect of the walls of the bottle. The opinions of *Rideal* (16), *Reiff* (17), *Brunner* (6) and *Norrish* (18) are essentially the same. *Reiff* proves, that, though the autoxidation takes place undoubtfully on the glass-walls, the positive catalyst is not the wall, but the humidity, traces of which are adsorbed on it, i. e., the polar water molecules, activating the oxygen molecules and the carbonyl group of the benzaldehyde. He proves experimentally that completely dried benzaldehyde does not oxidise practically in the dark.

But we have to add to this observation the comments of *Moureau, Duffraise* and *Radoche* (19) too. These authors have pointed out how difficult is to determine the rôle of water in autoxidation processes. The P_2O_5 generally used for drying is also a strong anti-oxygen. Other substances used for drying can also have an anti- or pro-oxygen effect. Experiments in this direction are all the more difficult, as the distillation, following the drying also affects the velocity of autoxidation of most materials. It has been observed that many materials oxidise more or less during distillation or warming, not to mention that in the course of distillation minimal traces of impurities can get into it. If we consider the frequent "inversion" of the anti-oxygen (anti-oxygen — pro-oxygen) too, it is rather difficult to decide, whether exclusively the effect of water was observed or changes of other factors also contributed.

Beside the initial activation a question still exists in autoxidation process and that is the initial induction period, which may be observed often on benzaldehyde too. The induction period is really characteristic for autocatalytic processes. The autoxidation of benzaldehyde can by no means be called a purely autocatalytic process. Only the first half of the

autoxidation time curve (absc. = time; ord. = ml consumed) has autocatalytic character, i. e., the beginning part; the rest of the curve shows on the contrary a reaction of "autoinhibition" type.

Many investigators have tried to explain both parts of the curves, but arrived at contradictory results. In respect to the induction period there are really two opposing hypotheses.



According to *Berl* and *Winnacker* (4) the time of induction period is necessary for the formation of a stationary concentration of some positive — in all probability peroxide-like — catalyst. To prove their theory they demonstrated experimentally that in the autoxidation of benzaldehyde perbenzoic acid previously added shortens the induction period, while benzoic acid lengthens it. This means, in other words, that the perbenzoic acid catalyses and the benzoic acid inhibits autoxidation. As opposed to this *Bäckström* (20) and *Almquist* and *Branch* (14) attribute the existence of the induction period to the presence of traces of impurities, for they could not observe an induction period during autoxidation in properly purified benzaldehyde. *Duffraise* and *Chovin* (21) unite the two theories, attributing the cause of the induction period to the presence of perhaps undemonstrable impurities, which are gradually decomposed in the course of autoxidation, oxidised by peroxides or in other way. It is not decided, which of these theories is the most appropriate to the real circumstances.

Still more contradictory are the theories concerning the final phase of autoxidation with abruptly diminishing velocity. The opinions of the authors agree only in that the decrease in the velocity of autoxidation is much greater than could be explained on the basis of the law of mass action by the decrease in the concentration of benzaldehyde.

Raymond (5) as well as *Almquist* and *Branch* (14) explained the decrease of velocity by supposing the formation of anti-oxygens during autoxidation. According to *Raymond*, this anti-oxygen is the perbenzoic acid itself. He considers his conception proved by his experiments, when during autoxidation the velocity decreased rapidly, he destroyed the per-acid by heating and the reaction was continued at its original velocity. This statement, that per-acid is an anti-oxygen stands in sharp contradiction to *Berl* and *Winnacker* (4) who, as we saw, showed per-acid to be a positive catalyst. The same is established by *Duffraise* and *Chovin* (21), who found that all peroxides of oxygen, including ozone *(Briner* (22)*)* are excellent pro-oxygens. *Brunner* (6) attributes the great slowing down to the inhibiting effect of benzoic acid formed during the autoxidation. Namely, the benzoic acid formed adsorbs selectively on the active centers of the walls of the bottle and pushes out the benzaldehyde molecules. *Reiff* (17) seeks the cause of the phenomenon in the mechanism of autoxidation itself. There is evidence, that the process takes place in two steps. The first reaction, the formation of the perbenzoic acid occurs rapidly and it is exclusively oxygen-consuming. The second step, the decomposition of the per-acid is a slow process and is not accompanied by oxygen absorption. While only per-acid accumulates, the velocity of the over-all reaction is great. When this begins also to decompose the velocity of the over-all reaction diminishes gradually. Consequently the more benzoic acid is present during autoxidation, the greater is the decrease in velocity, thus indirectly the inhibiting effect of the benzoic acid can also be explained.

In respect to the effect of solvents, *Raymond* (5) states that the velocity of autoxidation of dissolved benzaldehyde is always decidedly less than that of pure benzaldehyde. He carried out experiments in methyl-cyclohexane and as a result he reported, that with the same quantity of aldehyde the velocity of autoxidation changed in direct proportion to the concentration. According to *Brunner*'s investigations (6), the solvents inhibit autoxidation and this inhibitory effect appears in an induction period. In the same solvents the induction period grows with increased dilution. *Brunner* used benzene and cyclo-hexane as solvents. Cyclohexane has a stronger inhibitory effect than benzene, according to *Brunner*, probably because it is more viscous and the diffusion of oxygen is slower. *Berl* and *Winnacker* (4) added different organic solvents to benzaldehyde in a 20% quantity; they also found, that all solvents reduce the velocity of autoxidation of pure benzaldehyde. The inhibitory effect increases in the following order: benzene → hexane → acetone → cyclohexane → ether → cyclohexene → alcohol.

As it may be seen, we have consistent experimental observations on the inhibitory effect of solvents on autoxidation. But this inhibitory effect has not been explained theoretically yet.

B) *Own Experiments.*

For our experiments we chose benzaldehyde as substratum. We could also have measured the effect of varying quantities of catalyst on benzaldehyde "in substantia" — of course only relatively, as benzaldehyde itself oxidises fairly rapidly. Considering that we wanted to carry out our experiments in a given apparatus, in semi-micro dimensions, it was necessary to dissolve the benzaldehyde in a solvent so that, in these circumstances, with proper dilution, such quantities of benzaldehyde could be added, that the calculated oxygen-consumption could be measured at our experimental conditions. The data on solvents found in the literature made their use still more natural for us. We supposed, that using solvents with the proper dilution we could succeed for the time of one autoxidation experiment in reducing the autoxidation velocity of benzaldehyde practically to zero, while affected by a catalyst the autoxidation under identical conditions occured at the due velocity and the absolute value of the catalytic effect itself could be measured.

But to carry out this conception experimentally seemed to be a rather difficult task. We had to choose a solvent which itself did not consume oxygen, either with or without catalyst; this solvent had to inhibit the autoxidation of benzaldehyde, but only to such a degree that it could be overcome by some catalyst and the process set going.

To solve the problem we first sought a suitable dilution, where differences in the inhibitory effects of the different solvents could readily be observed. Then in solvents which had relatively slight inhibitory effect, by reducing the concentration we tried to obtain, that oxygen absorption should not take place inside 2—3 hours. In the following step we sought a suitable catalyst, affected by which the autoxidation took place under these conditions during the same or a still shorter time.

For this series of experiments, consisting of 6—8 parts, we used large-surfaced adsorption catalysts, the activity of wich greatly fluctuated in the course of time and often underwent very great changes. To obtain reliable results it was therefore necessary to carry out a coherent series of experiments in the shortest time possible. We therefore tried to arrange our experimental conditions so that the absorption time of one autoxidation curve was not too long and for this reason we also restricted the study of the effect of the solvents and later of the catalysts to a fixed time (2—3 hours).

Selection of the solvent.

In the first series of experiments the effects of 9 solvents (no autoxidation in themselves) were compared under completely identical conditions (the same temperature, pressure, volume, stirring) in a 50% solution, at two temperatures, 13° and 23° C.

In the 50% solution the relative difference between the inhibitory effect of the solvents was more easily to be observed at both temperatures. The results are shown in Figures I/a and I/b (Table 1/a—1/b). From them it appears that:

a) at 13° all the solvents — in agreement with the literary data — have an inhibitory effect on the autoxidation of benzaldehyde. Nitrobenzene, 96% alcohol, glacial acetic acid and acetone had the greatest inhibitory effect, carbon tetrachloride the weakest.

b) The series of experiments carried out at 23° C led to results already essentially divergent. This divergence appeared not only in the increased velocity which accompanied the higher temperature, but the inhibitory effect of the solvents was also changed. The inhibitory effect diminished in the following order: nitrobenzene and alcohol had the strongest inhibitory effect, then dioxane → toluene → ethyl acetate → benzene → carbon tetrachloride → glacial acetic acid. Acetone, opposed to the literature, had only a weak catalytic effect, but this appeared only after an induction period. In the other solvents there was scarcely any induction period.

As appears from comparison of the two Figures (I/a and I/b), the nitrobenzene and alcohol solutions showed no oxygen absorption at either temperature. Glacial acetic acid and acetone, on the contrary, which had a very powerful inhibitory effect at 13° C, at 23° C scarcely retarded the process, but catalysed.

The dielectric constant of the four last-mentioned solvents (nitrobenzene, alcohol, acetone and glacial acetic acid) diminishes in the order of nomination, but is in order of size greater than that of the other solvents, excepted the ethyl acetate. From this it appears that the polar molecules are the most strongly inhibitory and that this effect changes mostly under the infleunce of temperature. As the carbonyl group of benzaldehyde is also polar, solvatation takes place in the latter polar solvents. There is evidence, that in this case the inhibitory effect can be explained by the formation of solvate sphere, the thickness of which decreases somewhat at higher temperatures. It is known of glacial acetic acid moreover that at lower temperatures its molecules are associated and these also decompose at higher temperatures. It can be imagined that this phenomenon also

affects the great decrease in inhibitory effect of glacial acetic acid at higher temperatures.

The above effect of temperature change can be brought into close relationship with the statements of *Taylor* (23) and *Dhar* (24), according to which the temperature coefficient of negative catalytic processes is in general decidedly greater than that of the positive, viz. non-catalytic processes. These two authors explain this phenomenon by the formation of "additional products" between the molecules of the inhibitor and substratum. In the opinion of *Duffraise* and *Chovin* (21), however, the rising temperature gradually destroys the anti-oxygens. Applying *Taylor* and *Dhar*'s general statements to our results, it is possible that the additional products of *Taylor* are solvated benzaldehyde molecules, while the solvate sphere consisting of anti-oxygen — according tu *Duffraise* and *Chovin*'s theory — gradually decomposes with a rise in temperature.

Of course the effect of the different solvents on the velocity of autoxidation cannot be explained by this one factor, for there are many others which influence the effect of the solvents (molecular structure, solubility, viscosity, etc.).

Investigating the relative difference in the inhibitory effect of the solvents, we had to deal with increased dilution. We therefore studied the effect of the solvents at 23° C in a 10% solution (1 ml benzaldehyde + 9 ml solvent). We found that in this dilution oxygen absorption did not occur in a single solvent during the time of the experiment (Table 1/c). As, according to *Brunner* (6), with greater dilution the induction period lengthens, our period of observation could also be considered merely a protracted induction period.

As mentioned above, for our further experiments we wanted to use solvents of relatively slight inhibitory effect. On the basis of previous investigations and reflections, carbon tetrachloride was considered the most suitable for this purpose.

It must be noted that all these investigations were merely informative experiments. We were fully aware of the fact, that from such experiments, carried out in the absence of a catalyst, a reliable conclusion could not be drawn with regard to the catalytic process itself. That is to say, the different solvents not only themselves exert different positive or negative catalytic effect, but they influence to a great extent and differently the effectiveness of foreign catalysts. But, justified by our later experiments, in the presence of catalysts too, carbon tetrachloride proved to be the most suitable solvent.

Selection of the catalyst.

We next investigated whether in a 10% carbon tetrachloride solution — where during the time of the experiment autoxidation did not take place at all without catalyst — the process would occur as effect of some catalyst and, if so, at which velocity.

As we have already seen, most investigators consider the initial activation of benzaldehyde autoxidation to be a heterogeneous catalytic process. If, however, the bottle wall acts as catalyst, then the addition of materials having large surface area must strongly increase the catalytic effect. This has been proved by *Reiff* (17) with silica sand and glass powder and by *Brunner* (6) with glass powder and pumice, which have large surface areas. All these materials have a strong catalytic effect. *Wieland* (25) used *Pd* and *Pt* catalysts of large surface for the autoxidation of benzaldehyde. He states that *Pt*- and *Pd*-black strongly catalyse the autoxidation of pure undissolved benzaldehyde.

On the basis of these data we attempted to accelerate with different *Pt* and *Pd* catalysts the autoxidation of benzaldehyde, inhibited by solvents.

In the second series of experiments (Figure II/a, Table 2/a) we studied the effect of *Pt*-black and on the other hand of *Pt* and *Pd* catalysts precipitated on carriers, in a 10% benzaldehyde solution in carbon tetrachloride (1 ml benzaldehyde + 9 ml CCl_4).

We first examined whether the carriers themselves did not exhibit a catalytic effect. *Wieland* (26) states that pure bone black, because of its strong adsorption, catalyses the autoxidation of benzaldehyde almost as vigorously as *Pt*- or-Pd-black.

We investigated the effects of the following carriers and supported catalysts:

Carriers: *a)* bone-black
b) barium sulphate

Supported catalysts:

a) Pt and *Pd* on bone-black
b) Pt and *Pd* on $BaSO_4$.

We used fairly large quantities of catalysts and carriers (20—40% of the quantity of benzaldehyde employed). If the results were negative we tried to get a result by increasing the amount of catalyst.

1. *Platinum black.* We first investigated the catalytic effect of *Pt* black on the basis of *Wieland*'s instructions (25). Autoxidation occured in a 10% solution in CCl_4 on the addition of 0,2 g *Pt*-black. So the *Pt*-black not only catalyses the benzaldehyde autoxidation without solvent, but

in spite of the solvent's inhibitory effect as well. However, as may be seen from Figure II/a, this catalytic effect of the 0,2 g *Pt* black appeared only after a very long induction period.

2. *Carriers.* We first investigated the catalytic effect of 0,4 g bone-black, but with negative results. During 4 hours of observation no oxygen was absorbed. Therefore for the present we only could conclude that bone-black does not act as a catalyst in a solvent. We obtained similar results with barium sulphate too. No consumption of oxygen took place during 4 hours of observation as effect of 0,4 g barium sulphate.

3. *Supported catalysts.* Precipitating *Pt* and *Pd* on the carriers mentioned above we studied the effects of the supported catalysts.

A) *The Pt and Pd catalysts on bone-black* contained 5% *Pt* and *Pd* respectively. We made two experiments with both catalysts. To each of the solutions of 10% benzaldehyde the following quantities of catalysts were added:

0,4 g *Pt* catalyst on bone-black
1,0 g „ „ „ „ „
0,4 g *Pd* „ „ „ „
1,0 g „ „ „ „ „

but during 2 hours' observation we could not remark oxygen consumption in any case. So not only pure bone black, but also *Pt* and *Pd* precipitated on bone black failed to exhibit a catalytic effect.

B) *Pt and Pd precipitated on barium sulphate* (5% catalyst). 0,4 g of these catalysts was used in an experiment. *Pd on $BaSO_4$ proved to be an excellent catalyst.* The autoxidation occured after a few minutes' induction period at a high velocity. *Pt* on $BaSO_4$ also catalysed the process, but decidedly less, than the *Pd*. $BaSO_4$ is therefore a much more useful carrier for autoxidation catalysts than bone-black.

On the basis of these data the problem arose whether the bone-black did not catalyse only the autoxidation of benzaldehyde, or was anti-oxygen in general. We made two experiments to solve this problem:

1. 0,2 g bone-black was added to 5 ml pure (i. e. undissolved) benzaldehyde.

2. 0,2 g *Pd* catalyst on $BaSO_4$ and 0,2 g bone-black were added to a 10% solution of benzaldehyde in CCl_4 (Figure II/b, Table 2/b).

In the first case the rate of autoxidation of pure benzaldehyde diminished greatly affected by bone-black, in the second case the autoxidation was completely inhibited by bone-black, though it occured very rapidly with *Pd* catalyst on $BaSO_4$: no oxygen consumption occured in 3 hours.

These results show that *bone black is a fairly strong antioxygen* and are in sharp contradiction to *Wieland*'s statement (26), which attributes a strong pro-oxygen effect to bone-black. It must be noted that *Brunner* (6) who likewise investigated the catalytic characteristics of blood black in the auoxidation of benzaldehyde, came to similar conclusions. He could give not explanation of the phenomenon, however.

From all these results we can establish that for carrying out our investigations *Pt* black and *Pd* precipitated on barium sulphate will be suitable as catalysts.

Autoxidation experiments with Pd on $BaSO_4$ in different solvents.

Before studying the effect of the amount of catalyst we wanted to be convinced whether in the presence of the *Pd* on $BaSO_4$, which has been proved to be the best catalyst, CCl_4 will be the most suitable medium also for these experiments, because from the effect exhibited by the solvents without a catalyst reliable conclusions could not be drawn to the effect developed in the catalytic process.

For this reason comparison was made in the third series of experiments, now in the presence of the catalyst, between the effects of the 9 solvents previously investigated, in the same dilutions (10%), with the same quantities of *Pd* catalyst on $BaSO_4$. From the results as shown in Figure III (Table 3) it may be seen that CCl_4 is really the most suitable medium. Excepted CCl_4 the process could be carried out only in glacial acetic acid at the proper rate, but only after a very long induction period. It must be noted that the alcohol under the effect of the catalyst consumed itself oxygen at a fairly high velocity and therefore, apart from its inhibitory effect, it could not be employed as solvent in autoxidation experiment of this kind where a catalyst is also present.

Autoxidation of benzaldehyde with platinum black catalyst.

After establishing the circumstances of the autoxidation, we wanted to study in our experiments the effect of varying quantities of the catalyst on the rate of autoxidation. In autoxidation experiments the oxygen consumption cannot be presumed exactly. The autoxidation of benzaldehyde — as it has been established by *Baeyer* and *Villiger* (12) — takes place in two steps. If only benzoic acid should be formed from the benzaldehyde, there would be an oxygen consumption of $^1/_2$ mol, which in the case of 1 ml benzaldehyde would correspond to 120 ml oxygen. If, however, perbenzoic acid should be formed, the oxygen consumption would be twice as much, i. e. 240 ml. The perbenzoic acid primarily formed, however,

sooner or later — depending on the experimental conditions — changes to benzoic acid, but only to a certain extent, probably until equilibrium is reached. At the end of the autoxidation, that is, after the complete transformation of the benzaldehyde, therefore, we get benzoic acid and perbenzoic acid as terminal products. Consequently the oxygen consumption, depending on the amount of per-acid decomposed during the experiment, will fluctuate between

$^1/_2$ mol O_2 (120 ml) for 100% benzoic acid and
1 mol O_2 (240 ml) for 100% perbenzoic acid.

In view of these circumstances in parallel experiments we always compared uniformly the time necessary for the absorption of 120 ml O_2, all the more as here the curves often fall abruptly and the great slowing down occured only after the absorption of 120 ml. The time necessary for the absorption of 120 ml O_2 will be termed as the *"oxidation time"* and the quantity of O_2 absorbed over 120 ml *"over consumption"*. Beside the "oxidation times" we have also usually given the times required for the absorption of 90, 60 and 20 ml O_2 and have termed them the "3/4, $^1/_2$ *and* $^1/_6$ *oxidation times"*.

From the fourth series of experiments carried out with platinum black catalyst, it appears (Figure IV, Table 4), that in a 10% benzaldehyde solution in CCl_4 on changing the amount of catalyst, in otherwise identical conditions (the same temperature, pressure, stirring) *the oxidation time does not change linearly with the quantity of catalyst, but passes through a maximum and minimum.* We therefore succeeded in proving in this series of experiments already that in autoxidation processes — at least formally — the same phenomenon can be observed as *Csűrös, Zech* and *Géczy* (7) experienced in connection with catalytic hydrogenation.

From the different time curves it may be seen that with *Pt* black catalyst autoxidation often occurs only after a very long induction period. The length of these induction periods, during which there is no oxygen consumption at all, could not always be reproduced exactly, though the velocity of autoxidation following the induction period could be determined. We therefore compared the autoxidation velocities observed with different quantities of catalyst by taking the oxidation time, or its fractions, from the end of the induction period into account. The duration of the induction period in this case, as well as in the later series of experiments, was also determined graphically by extending the curve to the abscissa.

The *Pt* black as catalyst proved unsuitable for further investigations, not only because of the very long and unreproducible induction periodes

but also because the activity of the catalyst decreased in a relatively short time so rapidly that it was useless for further measurements.

Autoxidation of benzaldehyde with Pd catalyst precipitated on $BaSO_4$.

In the fifth series of experiments the effect of varying quantities of *Pd* catalyst on $BaSO_4$ was investigated, likewise in a 10% solution in CCl_4. Of the curves taken with this catalyst, not only the part following the induction period could be reproduced within the limits of experimental error, but the induction periods themselves too. The results are shown in Figures V, V/a and V/b and in Table 5/a.

It appears in Figure V., that the duration of the induction period was short — the maximum 14 minutes (18% of the oxidation time) — as opposed to one often lasting over an hour with the *Pt* black catalyst (80% of the oxidation time). It may also be seen in the Figure furthermore that with varying quantities of catalyst the "over consumption" also varied.

According to Figures V/a and V/b the oxidation time curve passes in this case too through a minimum and maximum changing the quantity of the catalyst. This phenomenon is not affected by counting the time required for the absorption of 120 ml O_2 from the beginning or the end of the induction period. We get the same result on any action of the autoxidation curve also when varying quantities of catalyst we compared the times necessary for the absorption, not of 120 ml, but of 90, 60 or the first 20 ml of O_2. But the smaller was the number of ml used for comparison, the flatter the extreme values became.

With *Pd* catalyst on $BaSO_4$ it was possible to find a relationship between the quantity of catalyst and the time of the induction period: *on increasing the quantity of catalyst the length of the induction period slowly diminished.*

Considering that we observed varying amounts of over consumption with different quantities of catalyst, which at the same time proves the presence of different quantities of per-acid, the question arose to what extent the catalyst itself and changes in its quantity affected the formation and decomposition of the per-acid. According to *Raymond* (5) and *Brunner* (6), the catalysts in the heterogeneous phase promote the first process exclusively, i. e., the formation of per-acid and exhibit no influence on the second process, on the decomposition of per-acid which, in their opinion, takes place in the homogeneous phase.

To clear up the question we determined analytically, in case of varying quantities of catalyst, the amount of perbenzoic acid formed at

two points of the autoxidation curve and, as a control, the total acidity. One series of determinations was made after the cessation of autoxidation, the other, in a new series of experiments, — interrupting the autoxidation — after the absorption of 120 ml O_2 (Series V/a—V/b).

Within the limits of experimental error the percentual quantities of perbenzoic acid and benzoic acid always produced 100% (as of the benzaldehyde in question). The sum of the oxygen consumption corresponding to the quantities of the two substances calculated theoretically likewise agreed well, within the limits of experimental error, with the total O_2 consumption observed in the practice.

Both series of experiments brought identical results (see Figures VI/a, VI/b; Table 5/a, 5/b), namely *with changes in the quantity of catalyst a sharp selectivity was shown.* The amount of per-acid was at the minimum where the oxidation time was at maximum. In Figure VI/b the amount of O_2 consumption is shown in percent corresponding to the values of per-acid analysed, taking the total O_2 consumption as 100%. Formally these results completely agree with the selectivity observed by *Csűrös, Zech* and *Pfliegel* (27) in catalytic hydrogenations. In hydrogenations the percentual saturation of the double bond varies according to the amount of catalyst in the same way as, in our experiments, the percentual amount of per-acid.

According to this and contrary to the opinions of *Raymond* (5) and *Brunner* (6), the catalyst and changes in its quantity, beside affecting the formation of per-acid, also influence its decomposition.

Changes in the quantity of the catalyst probably changes the velocity of the two steps in respect to each other and possibly affect the decomposition of the per-acid by reducing or increasing the over-all rate of autoxidation. With smaller quantities of catalyst the oxidation time is reduced fas more than the quantity of per-acid (see Figure VI). The latter diminisher sharply where the oxidation time shows a maximum and where this becomes shorter again the amount of per-acid increases rapidly. This section of the curve following the extreme values looks as if the final amount of per-acid would also be affected by the shortness or length of the oxidation time. In our opinion, where the over-all reaction is slow, the per-acid formed has longer time for decomposition and where the whole process is carried out rapidly the per-acid getting shorter time for decomposition may accumulate.

It is apparent that *in the course of autoxidation processes, at least formally, the same phenomena can be observed as in relation to catalytic hydrogenation: a minimum — maximum curve, depending on the amount of catalyst and selectivity.*

The chemical mechanisms of the two processes are different, but the experimental conditions and the system used for carrying out the experiments were the same for hydrogenation and autoxidation. (Substance dissolved + solvent = fluid phase; catalyst = solid phase; H_2 or O_2 = gaseous phase; stirring.)

The question thus naturally arose, whether the phenomenon was not caused by one or more physical constants common to both systems. *Csűrös* and *Popper* (28) observed in connection with catalytic hydrogenations, that with rapid stirring the extreme values appeared sharply, but with slow stirring they flattened out and on the basis of these observations they also raised the question of whether the cause of the phenomenon might not be the stirring itself, i. e., one of the physical constants of the system. The maximum—minimum curve can in all probability not be explained by a single factor, but is the result of the united action of several factors. It therefore seemed necessary to investigate the different constants of the system and first of all the effect of the solvent. The question was, whether the maximum—minimum curve would appear without solvent.

Influence of the solvent on the formation of extreme values.

We were unable to investigate the velocity of autoxidation in the absence of solvent beyond the initial velocity, partly because the experimental arrangements were of semi-micro dimension and partly because the solid benzoic acid precipitating later increased the viscosity to such extent that stirring was impossible. But in Figure V/a—b it may be seen that we got a minimum—maximum curve in a series of experiments made with solvent from comparison of the $^1/_6$ oxidation times too and we therefore supposed that without solvent it might also be determined from the initial velocities ($^1/_6$ oxidation time) whether they give the minimum—maximum curves with different quantities of catalyst. Of course, in the experiments made without solvent it was necessary to use larger quantities of benzaldehyde than in solvent, but at the same time the relative quantity of catalyst also had to be changed in proportion to the other greater quantities. In the solvent we used *Pd* catalyst on $BaSO_4$ containing 5% *Pd* to 1 ml benzaldehyde, without solvent at least 5 ml benzaldehyde had to be used. For this, therefore, either five times the quantity of the 5% catalyst had to be employed or a 25% catalyst equal in quantity to that used first.

Neither method was possible. We solved the problem in a new series of experiments by using, in the same quantity, a 1% catalyst to 1 ml benzaldehyde with solvent and a 5% catalyst to 5 ml benzaldehyde without solvent (Experimental Part, series VI and VII).

In solvent with 1% *catalyst* (Figure VII/a, Table 6) *we get the same result as with* 5% *catalyst* (see 6. series of experiments), the only difference being that the small quantities of catalyst (0,2, 0,3 g) catalysed very weakly and *the extreme values thereby shifted towards the greater catalyst quantities,* but, agreeing with the previous series of experiments, they also appeared in the fractions of oxidation time (90, 60, 20 ml) too. The 5% catalyst seemed to be somewhat more active than that of 1% prepared in the same way.

In the 7th series of experiments we investigated the initial autoxidation velocity of 5 ml "in substantia" benzaldehyde with varying quantities of catalyst. As in this case we could measure the catalytic effect only relatively, we offer for comparison, in Figure VII/b, the autoxidation velocity of 5 ml benzaldehyde to which no catalyst had been added. It is apparent that without catalyst there was no induction time, while as effect of the catalyst it occured in every case and decreased regularly with increasing quantities of catalyst. But the catalyst, in spite of the induction periods, increased the velocity of the autoxidation of "in substantia" benzaldehyde by at least 25%.

In Figure VII/a it may be seen, that with the increasing quantities of catalyst the $^1/_6$ oxydation time diminishes, then passes through an inflexion point, thereafter dropping slightly again (see Table 7). The inflexion point appeared at the same quantities of catalyst as the extreme values in the series of experiments carried out in solvent with 1% catalyst. *The extreme values obtained in solvent therefore shrink without solvent to an inflexion point,* which looks as if the solvent facilitated the formation of the extreme values.

Change in catalytic activity on varying the quantities of carrier added to the catalyst.

We also wanted to investigate in connection with the physical constants of the system to which extent the maximum—minimum curve was affected by the increased viscosity resulting from the greater mass of catalyst, which would affect the stirring, the surface and many other factors. We got perhaps no exact answer to this question, but we were able to observe a very interesting phenomenon from another standpoint.

We wanted to increase the mass of the catalyst by adding the $BaSO_4$ carrier which in itself has no catalytic effect. To supplement the amount of catalyst we always used the same $BaSO_4$. As we employed the catalysts on $BaSO_4$ only after storing them for a month, the carrier used to supply was also at least a month old. We had already found at the beginning of our

experiments that 0,4 g $BaSO_4$ did not exert a catalytic effect, but now, to make it certain, we investigated the effect of a greater quantity and found that the catalytic effect of 0,8 g $BaSO_4$ could also be considered practically zero.

The *IX/a "supplementory" series* was made in a 10% solution in CCl_4, always using 0,2 g *Pd* catalyst "B" on $BaSO_4$ (with 5% *Pd* content) and adding successively increasing quantities of carrier (0,1, 0,2, 0,3 g etc.). That is, *keeping the Pd content at constant value, we increased the total mass.* We observed the interesting phenomenon that already on the addition of 0,1 g $BaSO_4$ the velocity of the autoxidation increased greatly and *the oxidation time described a minimum—maximum curve with increasing quantities of carrier added to the same amount of supported catalyst in the same way as with increasing quantities of* 5% *pure catalyst when the Pd content also increased.* (See Figure VIII, Table 9/a.)

As we carried out this series of experiments with the much more active catalyst "B" — to be able to compare the experimental results with those of the series without supports — we repeated with catalyst "B" the fifth experimental series made with the less active "A" type. The oxidation times were decidedly shorter than with catalyst "A" due to the greater activity of catalyst "B", but the extreme values appeared at the same quantities of catalyst. (VIII. series of experiments; see Figure VIII, Table 8.)

From comparison of the two series of experiments made with the supplemented and pure catalyst it is also clear that in the supplemented series the extreme values shifted towards the smaller quantities and were somewhat flatter than in the series made with the pure catalyst. Otherwise in the supplemented series, just as in the unsupplemented, the extreme values also appeared in fractions of the oxidation time (see Tables 8 and 9/a).

In the *IX/b "supplemented" series* we proceeded by constantly increasing the quantity of catalyst, i. e., the *Pd* content, in each case supplementing with carrier to a constant quantity of 0,8 g. In the first experiment of the series we used 0,2 g catalyst + 0,6 g $BaSO_4$, in the last 0,8 g catalyst. In Figure VIII (Table 9/b) it may be seen that in spite of the increase in *Pd* content the oxidation time remained constant within the limits of experimental error. The induction period also gave a constant value.

It was difficult to evaluate these surprising results. It could be imagined that the inactive $BaSO_4$ acted as promoter or that the *Pd* activated the $BaSO_4$ (mixed catalysis). It is possible again that the phenomenon was

affected by change in the mass or factors in connection with it (surface, viscosity, etc.).

The results of the *IX/c "supplemented" series* argue against the promoter effect of the $BaSO_4$. In this series of experiments we investigated the process without solvent, otherwise in the same way as in the IX/a "supplemented" series, i. e., to a constant 0,2 g quantity of catalyst we added carrier in increasing quantities. As can be seen in Figure IX (see Table 9/c), we did not, however, observe an increase in catalytic effect on adding carrier; the oxidation time scarcely changed with the increased quantity of carrier, remained practically constant, contrary to the results of the VII. series, according to which, likewise without using solvent, on increasing the quantity of pure catalyst the oxidation time was much reduced. Without solvent, therefore, the phenomenon obeserved in solvent as effect of carrier could not be seen.

If mixed catalysis had caused the velocity-increasing effect of the carrier, then the *Pd* and $BaSO_4$ would have had to show an activation effect even without the presence of solvent, supposing that the activation was not promoted by the solvent. But the probability of the latter is very little.

In Table 9/a—b we present the percentual changes as related to the total mass of *Pd* content. In the IX/a supplemented series, where the amount of catalyst was kept constant and the total mass increased, the percentual quantity of *Pd* constantly decreased. In the IX/b experiments, on the other hand, it increased between the same limits (the *Pd* content increased inside a constant mass). If the minimum—maximum curve was caused by change in *Pd* content, then the two series would have had formally to result in about reciprocal curves. The fact is, on the conrary, that *in spite of increase in Pd content, with a constant mass we observed a constant velocity which shows that independently of the Pd content the mass or the surface determined the velocity.* If this proved to be true we could develop probably a correct explanation of the maximum—minimum curve as well.

SUMMARY.

The purpose of our experiments was to investigate whether in relation to autoxidation processes with heterogeneous catalyst the same phenomenon could be observed as was demonstrated by *Csűrös, Zech* and *Géczy* (7) in catalytic hydrogenations, where with changes in the quantity of catalyst the velocity of hydrogenation changes according to a maximum—minimum curve. Benzaldehyde was the model used for carrying out the experiments.

1. The conditions for autoxidation of benzaldehyde were investigated by:

a) selecting the most suitable solvent (CCl_4),

b) investigating the effects of *Pt* and *Pd* catalysts prepared in different ways. From these we chose *Pt* black and *Pd* on $BaSO_4$ for our experiments, as having the greatest catalytic effect.

2. It was demonstrated that bone black exerts a strong anti-oxygen effect on the autoxidation of benzaldehyde.

3. It was found that with changing quantities of *Pt* black and *Pd* on $BaSO_4$ catalysts the velocity of autoxidation changes according to a maximum—minimum curve. The *Pd* catalyst on $BaSO_4$ proved to be much better than the *Pt* black. The induction period shortens slightly with increasing quantities of the *Pd* catalyst on $BaSO_4$.

4. The quantities of perbenzoic acid and benzoic acid formed in the course of autoxidation were determined. With changing the quantity of catalyst a great degree of selectivity could be achieved: the quantity of perbenzoic acid was minimum, where the velocity of autoxidation is at its minimum too.

5. Among catalysts on $BaSO_4$ prepared identically but with different *Pd* content, those with greater amounts of *Pd* seemed to be more active. With catalysts of less *Pd* content the extreme values shifted towards the greater quantities of catalyst.

6. Experiments made without solvent, but otherwise under the same conditions as above showed that the extreme values observed in solvent as effect of the changing quantities of catalyst shrink without solvent to an inflexion point. The induction period likewise decreases with the increasing quantities of catalyst, which agrees with the experiments carried out in solvent.

7. We gradually increased the constant quantity of *Pd* catalyst on $BaSO_4$ by adding carrier substance into the CCl_4 solution. With these increasing quantities the rate of autoxidation changed according to a maximum—minimum curve in the same way as when the quantities of pure catalyst were increased, only the extreme values shifted towards the smaller quantities. Without solvent (the method otherwise the same) the oxidation time scarcely changed as effect of increasing quantities of carrier.

8. We supplemented a changing amount of catalyst with carrier, to a constant quantity in each case, in CCl_4 solution. In spite of the increase in *Pd* content the oxidation time remained constant. The induction period also remained constant.

EXPERIMENTAL PART.

Our experiments were carried out in semi-micro apparatus as used and described by *Csűrös, Zech* and *Géczy* (7), *Csűrös, Zech* and *Pfliegel* (27), *Csűrös* and *Gergely* née *Popper* (28) and *Csűrös* and *Sellő* (29) in hydrogenations. It was modified only insofar as a 200 ml gas burette was used instead of a 30 ml one. The experiments were carried out in the same way as in the works cited.

I. *Purification of the materials.*

a) *Benzaldehyde.* We used Heine & Co.' s purissimum benzaldehyde (chlorfrei) preparation. It was purified in vacuo and distilled in nitrogen atmosphere. We always purified only the small quantity of material required for 4—5 series of experiments and used it within two weeks after distillation.

The freshly distilled benzaldehyde must be shielded from air and light. Therefore we quickly poured it into 5—6 small-sized bottles with glass stoppers, filled them up immediately, then stoppled and closed with paraffin. They were put into a tin box and kept in a dark place. On opening each bottle we tried to use its content within 1—2 days. The bottle once opened was kept over till the next day in a vacuum desiccator covered with a black cloth. To open it it was filled with nitrogen from a Deville flask. The benzaldehyde thus purified and stored proved to be suitable for comparative experiments. We never observed with it induction period during "in substantia" oxidations, which — according to literary data (14) — is the characteristic of its purity.

b) *Solvents.* The solvents used were also of "purissimum" quality. They were always freshly distilled just before using.

II. *Preparation of the catalysts.*

1. *Pt black.* Prepared according to *Wilstätter* and *Waldschmidt—Leitz*'s (30) description.

2. *Pt on bone black.* After *Skita* and *Meyer* (31). Contained 5% metal.

3. *Pd on bone black.* After *Gattermann* and *Wieland* (32). *Pd* content 5%.

4. *Pd on* $BaSO_4$. After *Schmidt* (33). The catalyst marked "A" contained 5% *Pd.* There was also 5% metal in catalyst "B", but in preparing it we stirred it vigorously during the reduction and boiling, which increased the activity of the catalyst by about 20%, i. e., decreased the time of oxidation by about 20%.

The catalyst marked "C" was prepared in the same way but contained only 1% *Pd*.

5. *Pt on* $BaSO_4$. It was prepared in the same way as the *Pd* catalyst "B" on $BaSO_4$ with 5% *Pt* content.

III. *Analytical methods.*

We determined on the one hand the amount of perbenzoic acid formed during autoxidation, on the other hand the amount of perbenzoic acid and benzoic acid together, i. e., the total acidity.

When the autoxidation was finished we filtered the CCl_4 solutions into 50-ml normal flasks to free them from the solid catalyst. The bottle used for the experiment and the catalyst on the filter were thoroughly washed out 6—8 times with CCl_4, filled up again and thoroughly shaken. Immediately after filling them up we made the analysis to avoid possible decomposition of the per-acid. We always used 5 ml of the standard solution and employed the well known iodometric process (12, 14, 26). We added 0,5 g *KJ* to it in a glass-stoppered Erlenmeyer flask, made acidic with 10% *HCl* and shaking vigorously titrated the precipitated iodine with $n/10$ $Na_2S_2O_3$. We made blind tests before the determination in all cases with the reagents employed and CCl_4.

The iodometric titration gave entirely accurate results. The solution of $Na_2S_2O_3$ parallely consumed was generally the same to 0,01 ml. The calculated O_2 consumption corresponding to the quantity of per-acid obtained by analysis was within 5% less than twice the "over consumption" observed experimentally. The 5% limit of error in O_2 consumption can be attributed on the one hand to inaccuracies in the volumetric method and on the other hand it is possible that during autoxidation side reactions accompanied by a small percentage of O_2 consumption also take place, a thing also confirmed in the literature (14).

We found no literary description for determination of the total acidity in CCl_4. The following method was used, proved to be useful for achieving approximate results.

We distilled 5 ml of the standard solution in a 25 ml fractionating flask without a previous long boiling on a micro-Liebig cooler. The distillation residue (separate sample) taken up with CCl_4 or alcohol did not turn the *KJ* starch paper blue, that is, the per-acid is transformed but the CCl_4 distilling through carried off a little non-transformed per-acid: in the distillate we noted a slight J_2 precipitation. We therefore took up the distilling CCl_4 in a glass-stoppered Erlenmeyer flask. At the end of the distillation we washed out the Liebig cooler thoroughly 2—3 times

with CCl_4 into the collecting bottle, then titrated the perbenzoic acid iodometrically as above and added the values received to the results of the acidimetric titration as correction. After rinsing the side tube of the fractionating flask into the bottle itself with 96% ethyl alcohol we dissolved the distillation residue (benzoic acid) in alcohol and titrated it (phenolphtalein) with *N*/10 *NaOH* in the fractionating flask itself to avoid losses. The change was sharp, even taking into consideration the quantity of per-acid distilling through, the parallel analyses corresponded well. Taking the benzaldehyde used or the total O_2 consumption experimentally observed as 100%, the values calculated on the basis of these analysis approximate this with an average error of 5—6%. The CCl_4 and the alcohol used for the experiments were completely neutral.

IV. *Summary of the different series of experiments.*

First series of experiments.

Investigations on the effect of different solvents on autoxidation of benzaldehyde.

a) in 50% solution at 13° C

b) in 50% solution at 23° C

c) in 10% solution at 23° C

a—b) The 50% benzaldehyde solutions were prepared in each case by adding 2,5 ml solvent to 2,5 ml benzaldehyde. The total volume of the pure benzaldehyde, the O_2 absorption of which was investigated for comparison, was likewise 5 ml.

TABLE 1/a.

In 50% solution at 13° C. (See. Figure 1/a.)

Time in min.	O_2 absorp. of pure benzaldehyde, ml	O_2 absorption in different solvents in ml							Remarks
		Acetone	Glacial acetic acid	CCl_4	Benzene	Toluene	Ethyl acetate	Dioxane	
5	3,0	—	—	1,1	—	—	0,9	0,6	In alcohol, nitro benzene, acetone, and glacial acetic acid no O_2 absorption occured in 120 min.
10	5,9	—	—	2,3	—	—	0,9	0,8	
20	12,5	—	—	5,4	—	—	0,9	1,2	
30	18,2	—	—	7,1	0,3	0,0	1,2	1,7	
40	25,1	—	—	9,7	0,4	0,1	1,4	2,3	
50	31,3	—	—	13,2	0,6	0,1	1,5	2,8	
60	37,8	—	—	16,3	0,8	0,2	2,0	3,5	
70	44,2	—	—	19,4	1,1	0,2	2,1	4,1	
80	49,1	—	—	22,8	1,4	0,2	—	4,7	
90	56,3	—	—	25,9	1,7	0,3	2,7	5,4	
100	62,8	—	—	—	1,9	0,3	2,9	6,0	
110	68,1	—	—	—	2,1	0,3	3,5	6,7	
120	74,3	—	—	—	2,3	0,4	4,2	7,3	

TABLE 1/b.

In 50% *solution at* 23° *C.* (See Figure I/b.)

Time in min	O_2 absorp. of pure benzaldehyde ml	O_2 absorption in different solvents, in ml							Remarks
		Acetone	Glacial acetic acid	CCl_4	Benzene	Toluene	Ethyl acetate	Dioxane	
5	7,1	1,1	2,0	1,8	1,7	1,3	0,5	0,3	In alcohol and nitro benzene no O_2 absorption occured in 120 min.
10	13,2	5,6	8,0	4,0	4,8	2,0	1,3	2,0	
15	19,4	12,4	11,8	8,0	6,7	3,7	2,2	3,0	
20	26,3	21,3	17,6	12,1	10,0	6,1	4,3	3,9	
25	33,2	31,8	23,9	15,9	12,1	8,2	6,0	5,7	
30	39,1	41,7	31,0	20,0	14,1	10,0	7,0	6,0	
35	45,8	49,0	38,7	24,4	16,3	12,0	8,2	7,3	
40	52,9	56,3	46,0	29,0	18,2	13,9	10,3	8,7	
45	59,6	64,0	53,8	33,1	20,4	15,0	11,8	10,1	
50	66,1	71,8	60,7	37,2	22,1	16,2	13,2	11,5	
55	73,0	78,5	68,2	42,0	23,9	17,9	14,7	12,6	
60	79,8	84,2	75,0	47,3	25,8	19,5	16,1	13,8	
65	85,9	91,0	82,1	51,8	27,0	21,0	18,0	15,0	
70	92,5	96,0	88,0	56,0	28,4	22,3	20,0	16,0	
75	100,2	102,3	94,2	60,3	30,0	23,8	21,5	17,0	
80	—	—	100,0	64,7	31,7	24,7	23,3	18,1	
90	—	—	—	72,8	34,0	27,0	26,0	20,2	
100	—	—	—	80,5	36,7	28,2	29,6	23,0	
110	—	—	—	88,8	40,0	30,0	31,8	24,3	
120	—	—	—	95,8	42,0	31,8	37,3	25,9	

1/c. The 10% benzaldehyde solutions were prepared by adding 9 ml of the different solvents to 1 ml benzaldehyde. The total volume was always 10 ml.

TABLE 1/c.

	O_2 absorption of 10% benzaldehyde solutions prepared with different solvents						
	Acetone	Glacial acetic acid	CCl_4	Benzene	Toluene	Ethyl acetate	Dioxane
Time observed in hours	2	2	4	2	2	2	2
O_2 consumption in ml	0	0	0	0	0	0	0

Second series of experiments.

2/a. *Investigations on the different Pd and Pd catalysts and carriers in a* 10% *solution of benzaldehyde in* CCl_4.

The solutions always contained 1 ml benzaldehyde and 9 ml CCl_4. The total volume was therefore 10 ml.

TABLE 2/a. (See Figure II/a.)

Time in min.	O_2 absorption observed with different catalysts			Remarks
	0,2 g *Pt* black	0,4 g *Pt* on $BaSO_4$	0,4 g *Pd* on $BaSO_4$	
5	—	—	0,7	O_2 absorption did not occur with the following carriers and supported catalysts:
10	—	—	4,0	
15	—	—	23,2	
20	—	—	40,0	
25	—	0,9	55,1	0,4 g bone black
30	—	2,7	70,1	0,4 g $BaSO_4$
35	—	6,7	84,6	(in 4 hours)
40	—	12,1	98,8	0,4 g *Pt* on bone black
45	—	17,7	112,6	0,4 g *Pd* on bone black
50	0,3	23,5	124,6	1,0 g *Pt* on bone black
55	11,0	28,9	136,6	1,0 g *Pd* on bone black
60	56,6	33,6	158,6	(in 2 hours)
70	97,4	42,9	170,7	
80	113,8	50,0	173,1	
90	126,0	57,0	173,2	
100	134,9	63,4	—	
110	142,0	69,2	—	
120	148,5	—	—	
130	153,1	78,8	—	
145	—	83,4	—	
165	—	92,3	—	
185	—	97,9	—	
205	—	102,3	—	
225	—	106,2	—	
245	—	109,4	—	

2/b. Anti-oxygen effect of bone-black.

Comparative experiments were made, two without solvent in a total volume of 5 ml and two in CCl_4 in a total volume of 10 ml.

TABLE 2/b. (See Figure II/b.)

Time in min.	O_2 absorption of 5 ml benzaldehyde, in ml		O_2 absorption of a 10% solution of benzaldehyde in CCl_4 as effect of 0,2 g *Pd* catalyst on $BaSO_4$, in ml	
	without bone black	with 0,2 g bone black	without bone black	with 0,2 g bone black
5	5,2	2,0	0,7	0,5
10	12,1	3,7	0,8	—
15	18,0	4,3	5,0	—
20	25,1	5,2	17,6	0,5
25	33,0	6,0	27,8	—
30	38,0	6,9	38,0	0,5
35	45,0	7,4	48,3	—
40	52,1	8,0	59,2	0,6
45	59,3	8,7	70,0	—
50	65,4	9,5	80,5	0,7
55	72,0	10,2	90,0	—
60	78,2	11,0	101,5	0,7
65	84,7	11,3	111,8	—
70	92,1	12,0	122,0	0,7

TABLE 2/b, **continued.** (See Figure II/b.)

Time in min.	O_2 absorption of 5 ml benzaldehyde, in ml		O_2 absorption of a 10% solution of benzaldehyde in CCl_4 as effect of 0,2 g *Pd* catalyst on $BaSO_4$, in ml	
	without bone black	with 0,2 g bone black	without bone black	with 0,2 g bone black
75	99,3	—	132,0	—
80	—	14,0	140,3	—
90	—	15,0	155,1	1,5
100	—	17,5	—	1,6
110	—	20,5	—	—
120	—	23,0	—	—
130	—	25,3	—	1,8
140	—	29,7	—	2,2
150	—	33,9	—	2,5

Third series of experiments.

Investigation on the autoxidation of 10% *benzaldehyde solutions prepared with different solvents, with Pd catalyst "A" on* $BaSO_4$.

The solution always contained 1 ml benzaldehyde and 9 ml solvent and the quantity of catalyst used was 0,4 g.

TABLE 3. (See Figure III.)

Time in min.	O_2 absorption of benzaldehyde in the different solvents in ml.					Remarks
	CCl_4	Glacial acetic acid	Dioxane	Benzene	Toluene	
5	2,5	0,2	0,1	—	—	The nitrobenzene, acetone and ethyl-acetate solutions absorbed no O_2 in 2 hours.
10	27,0	0,2	—	—	—	
15	48,1	—	—	—	—	
20	70,3	—	—	—	—	
25	89,7	—	0,3	—	—	
30	107,1	—	0,9	—	—	
35	124,2	—	1,5	—	—	
40	140,1	—	1,9	—	—	
45	154,6	—	2,5	—	—	
50	161,8	0,5	2,8	—	—	
55	168,0	1,6	3,5	—	—	
60	174,1	6,8	4,3	—	—	
65	177,4	20,5	5,2	—	—	
70	177,8	37,0	5,7	—	—	
75	—	51,7	6,0	—	—	
80	—	67,4	6,8	—	—	
90	—	93,0	8,1	—	0,2	
100	—	113,5	9,3	0,5	0,4	
110	—	129,1	9,8	2,0	0,7	
120	—	141,5	11,7	4,4	3,0	
130	—	150,7	12,9	7,9	5,3	
140	—	157,2	—	12,2	7,3	
150	—	162,2	—	14,1	9,1	
160	—	166,0	—	16,2	11,2	
170	—	168,5	—	19,5	13,3	
180	—	170,9	—	21,7	15,3	
190	—	172,2	—	24,9	17,3	
200	—	173,4	—	—	19,6	
210	—	174,0	—	—	20,1	
220	—	174,6	—	—	22,4	

Fourth series of experiments.

Effect of varying quantities of Pt black catalyst on the autoxidation of benzaldehyde.

The total volume of the benzaldehyde solution in CCl_4 was 10 ml in each experiment. The varying quantities of catalyst were suspended in 8 ml CCl_4, and into this, at the beginning of the experiment, we poured the mixture of 1 ml benzaldehyde and 1 ml CCl_4. The "oxidation time" given in the Table is taken into account from the end of the induction period.

TABLE 4. (See Figures IV/a—IV/b.)

Amount of catalyst in g	Total O_2 consumption in ml.	Induction period, in min.	Oxidation time in min., till		
			60 ml	90 ml	120 ml
			O_2 is absorbed		
0,10	176,3	79	14	24	36
0,15	161,6	20	9	17	32^{30}
0,20	160,7	34^{30}	7^{30}	12^{30}	18^{30}
0,25	161,4	30	8^{30}	16^{30}	26
0,30	163,8	90	7^{30}	13	22
0,35	164,4	62^{30}	5^{30}	9	16
0,40	153,5	54	4	7^{30}	14^{30}
0,50	145,0	54^{30}	3^{30}	6^{30}	12^{30}

Fifth series of experiments.

Effect of varying quantities of Pd catalyst "A" on $BaSO_4$ (5% Pd content) on autoxidation of benzaldehyde.

The varying quantities of catalyst were always added to 10 ml of the 10% benzaldehyde solution in CCl_4 (1 ml benzaldehyde + 9 ml CCl_4).

In *series a)* we also noted the "excess consumption" and thereafter analysed the oxidised mixtures.

In *series b)* the autoxidation was stopped after the absorption of 120 ml O_2 ($^1/_2$ mol) and then analysis was made.

From the results of the analysis we calculated the amount of O_2 consumed to form per-acid or benzoic acid and from this we show in the Table what percent of the experimentally observed O_2 was consumed to form per-acid or benzoic acid. In the Tables we show only the "oxidation time" calculated together with the induction period, since from this, by substracting the induction period, which is likewise given the oxidation time not including the induction period can easily be established. We proceeded thus in all the subsequent Tables. The induction periods given were established graphically.

TABLE 5/a. (See Figures V., V/a. b, VI/a, b.)

Amount of catalyst in g	Total O_2 consumption in ml	Induction period in min.	Oxidation time in min. till				O_2 consumption as calculated from analysis, in %		Total O_2 consumption as calculated from analysis, in %
			20	60	90	120 ml	per-acid	benzoic acid	
			O_2 is absorbed						
0,2	177,8	14	23	44	60	76	64,68	31,96	96,64
0,3	177,2	11	18	34^{30}	47^{30}	58^{30}	62,10	35,02	97,12
0,4	174,2	9	15	27	36^{30}	46	58,30	36,66	94,96
0,5	167,8	7^{30}	12^{30}	21^{30}	29^{30}	38^{30}	54,20	40,87	95,07
0,6	150,5	6	14	25	37	54	38,10	58,22	96,32
0,7	174,5	5^{30}	11	21	29	37^{30}	57,10	39,70	96,80
0,8	167,8	6	9^{30}	18^{30}	26	34^{40}	57,30	38,13	95,43

TABLE 5/b. (See Figure VI/a—b.)

Amount of catalyst in g	Total O_2 consumption in ml	Induction period in min.	Oxidation time, absorption of 120 ml O_2, in min	O_2 consumption calculated from anal, in %		Total O_2 consumption calculated from analysis, in %
				Per-acid	benzoic acid	
0,2	120	13^{30}	71^{30}	72,67	23,45	96,12
0,3	120	10^{20}	55^{40}	63,95	30,89	94,84
0,4	120	8^{30}	41^{40}	59,78	34,50	94,28
0,5	120	7	36^{30}	57,75	37,58	95,33
0,6	120	6	56	39,73	55,27	95,00
0,7	120	5^{30}	36^{20}	50,20	46,27	96,47
0,8	120	5^{30}	32^{30}	54,33	30,58	93,91

Sixth series of experiments.

Effect of various quantities of Pd (1%) catalyst "C" on $BaSO_4$ carrier on autoxidation of benzaldehyde.

In this series of experiments we changed the quantity of the 1% catalyst in 10 ml of 10% benzaldehyde solution in CCl_4 (1 ml benzaldehyde + 9 ml CCl_4).

TABLE 6. (See Figure VII/a.)

Amount of catalyst in g	Induction period in min.	Oxidation time in min., till			
		20 ml	60 ml	90 ml	120 ml
		O_2 is absorbed			
0,2	10	26	—	—	—
0,3	8	12^{30}	40	62	84
0,4	6	9	29	44	60
0,5	5^{30}	8	21	31	40
0,6	5^{30}	7	14	19	25^{15}
0,7	6	11	19^{30}	26	31
0,8	5^{30}	9	17	22	27
0,9	6	7^{20}	14	18	23

Seventh series of experiments.

Effect of various quantities of Pd catalyst "B" (5% Pd) with $BaSO_4$ carrier on autoxidation of benzaldehyde without solvent.

The total volume was 5 ml in each experiment of this series. To the catalyst prepared in the flask we poured 5 ml benzaldehyde at the beginning of the stirring. We stopped the experiment when 100 ml O_2 had been absorbed, since there was so much solid benzoic acid present, that it made further stirring impossible.

TABLE 7. (See Figure VII/a—b.)

	Benzaldehyde without catalyst	Benzaldehyde + *Pd* catalyst „B" on $BaSO_4$ in g								
		0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0
Absorption time for 100 ml O_2 in min	78	61	45	39^{30}	36	34^{30}	34^{30}	33^{30}	30^{45}	28
Induction period in min	0	34	20	15^{30}	12	10^{30}	8^{30}	8	7	6^{30}

Eighth series of experiments.

Effect of various quantities of Pd catalyst "B" (5% Pd) with $BaSO_4$ carrier on autoxidation of benzaldehyde, in solvent.

The total volume was 10 ml in every case. 9 ml CCl_4 was added to 1 ml benzaldehyde.

TABLE 8. (See Figure VIII.)

Amount of catalyst in g	Total O_2 consumption in ml	Induction period in min	Oxidation time in min., till		
			60 ml	90 ml	120 ml
			O_2 is absorbed		
0,2	184,2	12	39	55	70
0,3	181,5	9	31	43	54
0,4	175,2	7	22	29	37^{50}
0,5	170,0	6	16	22	28
0,6	156,6	5	20	30	45
0,7	163,4	5	17	23^{30}	32
0,8	165,1	4	10^{30}	15	20

Ninth series of experiments.

In this series of experiments we supplemented the different quantities of *Pd* catalyst "B" (5% *Pd*) with $BaSO_4$ to greater amounts in different ways with pure $BaSO_4$ carrier.

In the 9/*a "supplemented" series* we always used 0,2 g catalyst in 10 ml of a 10% solution in CCl_4 and increased its quantity successively with $BaSO_4$.

TABLE 9/a. (See Figure VIII.)

5% *Pd* catalyst on $BaSO_4$	$BaSO_4$	Percentual Pd-content in the total mass, in %	Induction period in min.	Oxidation time in min., till			Remarks
amount in g				60 ml	90 ml	120 ml	
				O_2 is sbaorbed			
0,2	—	5,00	15	45	58	72	6 ml O_2 was consumed in 3 hours as effect of 0,8 g pure $BaSO_4$.
0,2	0,1	3,33	11	19	24^{30}	30^{45}	
0,2	0,2	2,50	7	23^{30}	32^{30}	39^{15}	
0,2	0,3	2,00	6^{30}	21^{30}	29	36^{30}	
0,2	0,4	1,66	6	16^{40}	21^{50}	27^{20}	
0,2	0,5	1,43	5^{30}	13	17	23	
0,2	0,6	1,25	4	9	12^{30}	18	

In the 9/*b* "*supplemented*" *series*, constantly increasing the quantity of *Pd* catalyst on $BaSO_4$ we supplemented it in every case to a constant quantity with $BaSO_4$ carrier.

The experiments were made in 10 ml 10% benzaldehyde solution in CCl_4.

TABLE 9/b. (See Figure VIII.)

5% *Pd* catalyst on $BaSO_4$	$BaSO_4$	Percentual Pd-content in the total mass, in %	Induction period, in min.	Oxidation time, to absorb 120 ml O_2 in min.
amount in g				
0,2	0,6	1,25	4	18
0,3	0,5	1,87	4	19
0,4	0,4	2,50	3	18^{42}
0,5	0,3	3,12	3	19
0,6	0,2	3,75	3^{30}	19^{30}
0,7	0,1	4,37	4	19
0,8	—	5,00	4	19^{35}

In the 9/*c* "*supplemented*" *series* the supplement was made without using solvent, otherwise in the same way as in series 9/a, that is, we increased the constant, 0,2 g quantity of catalyst by adding to it successively greater quantities of carrier. We used 5 ml benzaldehyde for all experiments. At the beginning of the stirring we poured it into the flask containing the catalyst with the carrier added to it.

TABLE 9/c. (See Figure IX/a.)

Pd catalyst on $BaSO_4$ g	0,2	0,2	0,2	0,2	0,2	0,2	0,2
+ $BaSO_4$ g	—	0,1	0,2	0,3	0,4	0,5	0,6
Time required for absorption of 100 ml O_2 in min	57	56	54^{15}	53^{45}	55^{30}	57^{10}	57^{30}
Induction period in min	33	29^{30}	27	25	24^{30}	24^{30}	25

In the *appendix to Table* 9/c it may be seen that the autoxidation velocity of 5 ml "in substantia" benzaldehyde diminished on the addition of $BaSO_4$.

APPENDIX TO TABLE 9/c. (See Figure IX/b.)

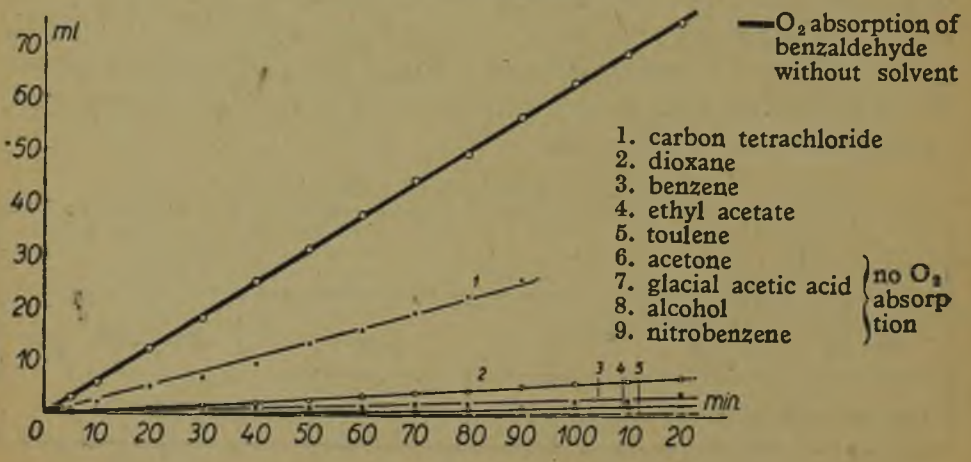
	O_2 absorption of 5 ml benzaldehyde		Remarks
	without $BaSO_4$	with 0,4 $BaSO_4$	
Time required for absorption of 80 ml O_2 in min ..	62	90	In this case the benzoic acid was already precipitated after absorption of 80 ml O_2.

Figure I.

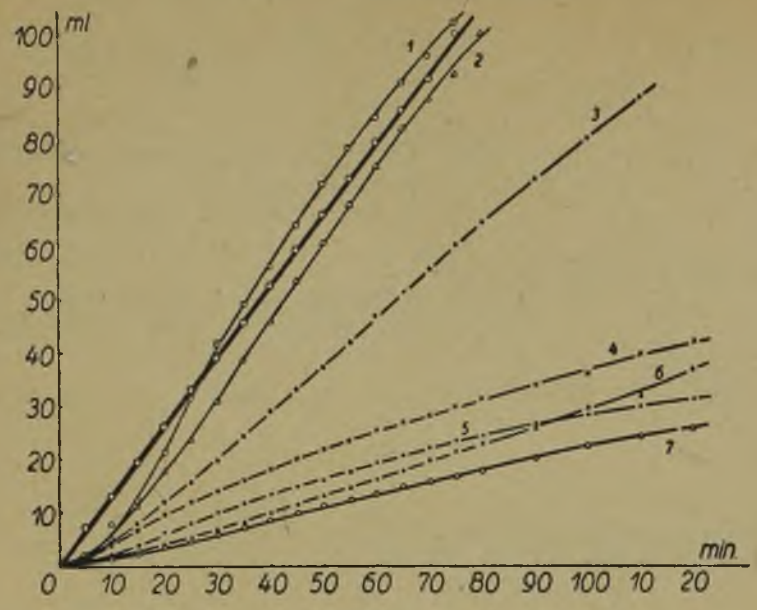
EFFECT OF DIFFERENT SOLVENTS ON THE AUTOXIDATION OF BENZALDEHYDE (in 50% solution).

(See Table I.)

a) 13° C (See Table I/a)



b) 23 C⁰ (See Table I/b)

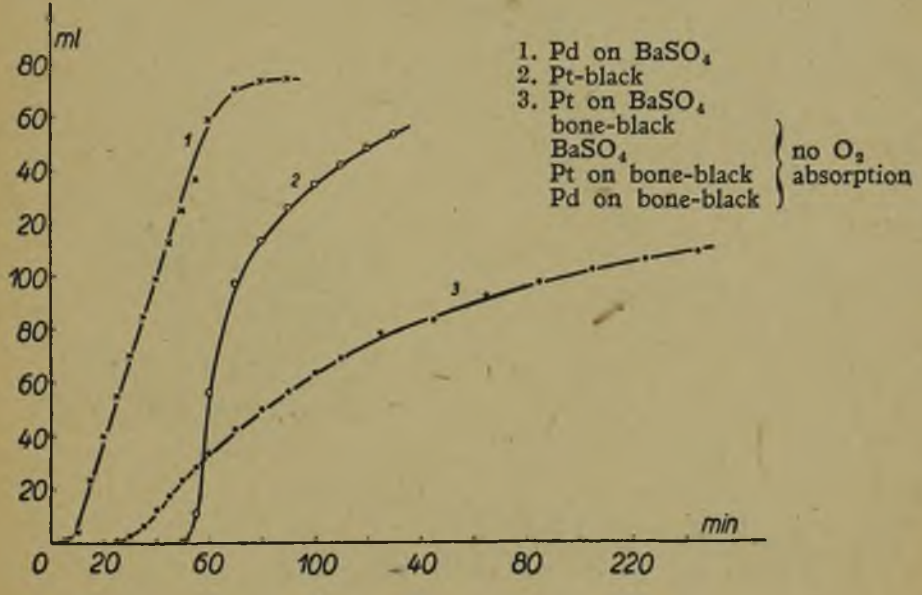


1. acetone
2. glacial acetic acid
3. carbon tetrachloride
4. benzene
5. toluene
6. ethyl acetate
7. dioxane
8. alcohol } no O_2
9. nitrobenzene } absorption

Figure II.

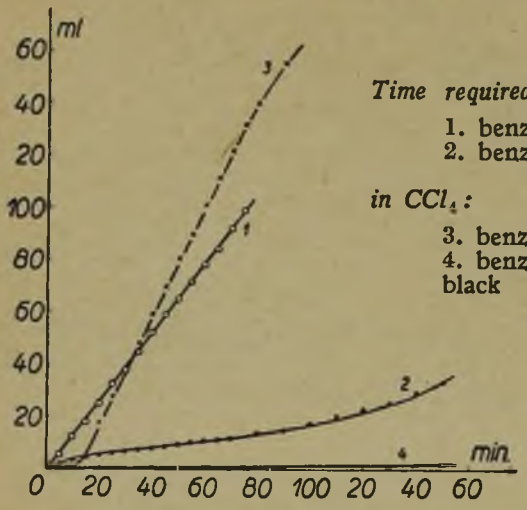
a) COMPARISON OF DIFFERENT Pt AND Pd CATALYSTS in a 10% solution of benzaldehyde in CCl_4.

(See Table II/a)



b) ANTI-OXIGEN EFFECT OF BONE-BLACK.

(See Table II/*b*)



Time required for O_2 absorption without solvent:

1. benzaldehyde
2. benzaldehyde + bone black

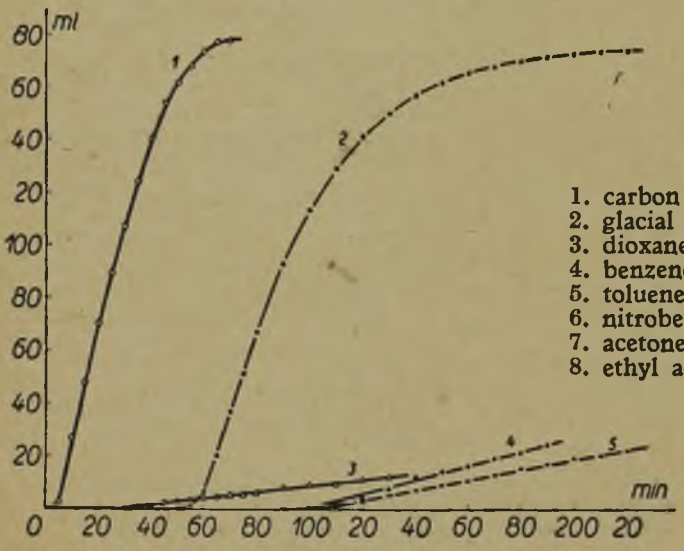
in CCl_4:

3. benzaldehyde + Pd on $BaSO_4$
4. benzaldehyde + Pd on $BaSO_4$ + bone black

Figure III.

AUTOXIDATION OF 10% BENZALDEHYDE IN DIFFERENT SOLVENTS, with Pd Catalyst "A" on $BaSO_4$.

(See Table III.)



1. carbon tetrachloride
2. glacial acetic acid
3. dioxane
4. benzene
5. toluene
6. nitrobenzene
7. acetone
8. ethyl acetate

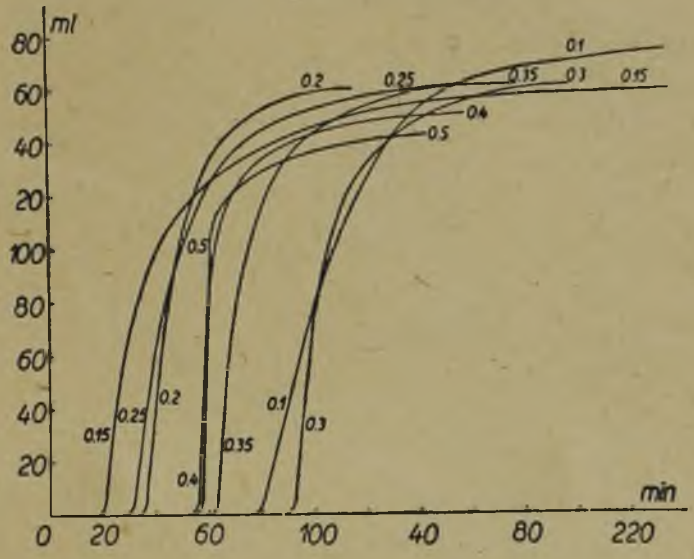
} no O_2 absorption

Figure IV.

AUTOXIDATION OF BENZALDEHYDE IN CCl_4 SOLUTION
with varying quantities of Pt black catalyst.

(See Table IV.)

a) Time required for O_2 absorption:



b) Oxidation time as function of the quantity of catalyst:

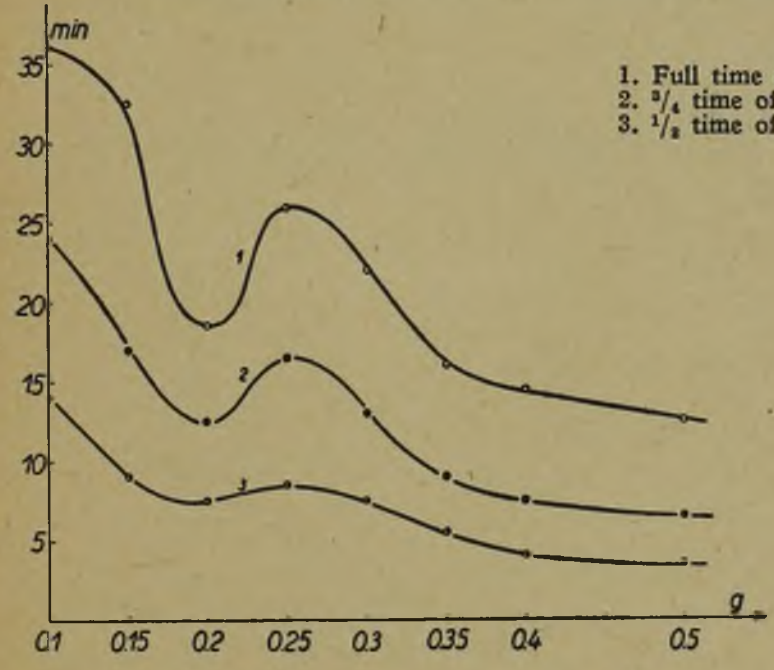
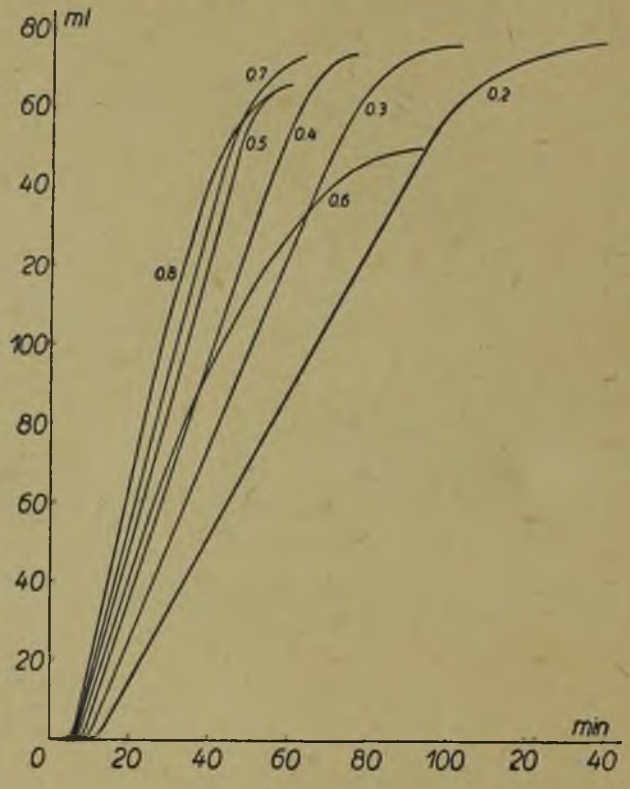


Figure V.

AUTOXIDATION OF BENZALDEHYDE IN CCl_4 SOLUTION
with Pd catalyst "A" on $BaSO_4$.

(See Table V/a)

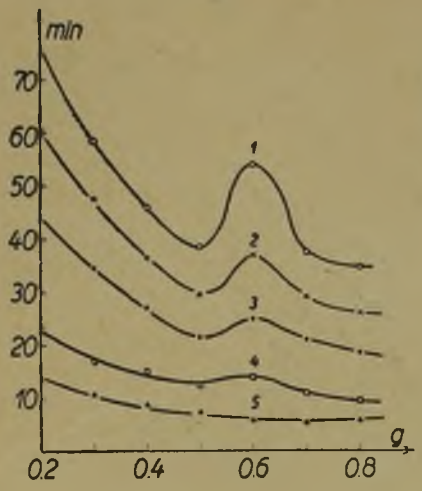
Time required for autoxidation.



TIME OF OXIDATION AS FUNCTION OF THE QUANTITY OF Pd CATALYST "A" ON $BaSO_4$.

(See Table V/a.)

V/a. Time of oxidation including induction period.



1. $^1/_1$ oxidation time
2. $^3/_4$ oxidation time
3. $^1/_2$ oxidation time
4. $^1/_6$ oxidation time
5. induction period

V/b. Oxidation time without induction period.

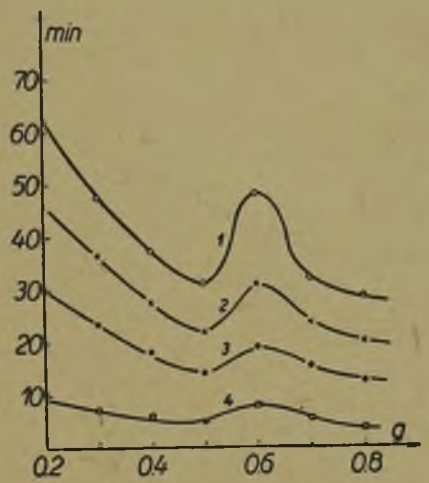
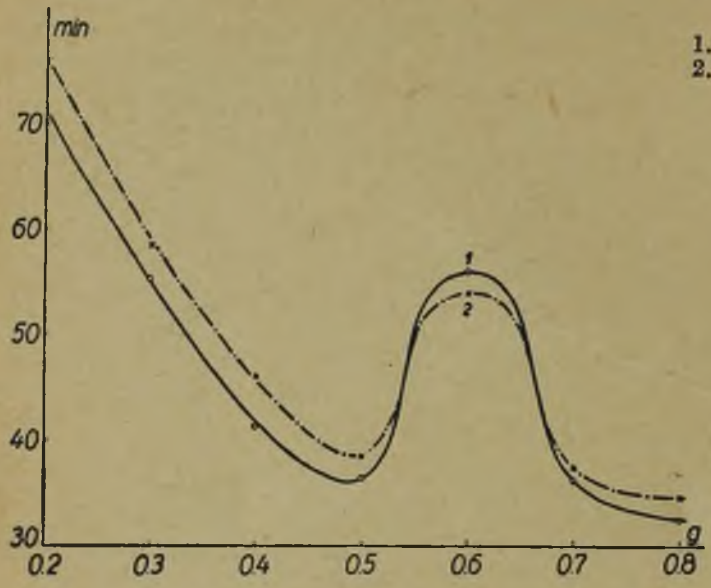


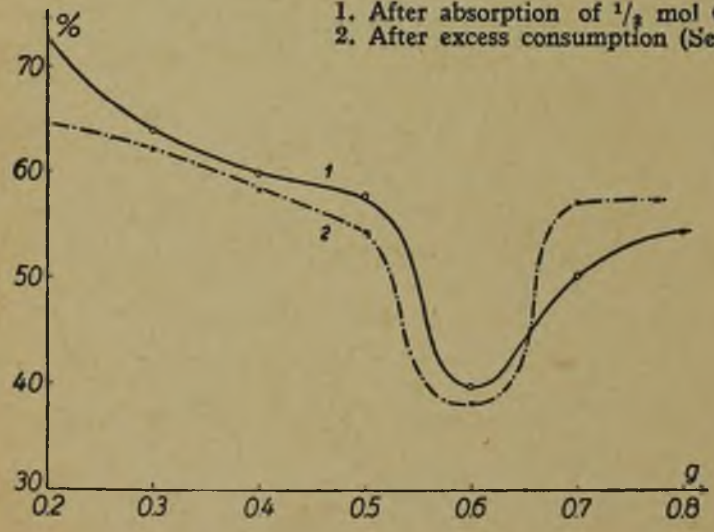
Figure VI.

a) OXIDATION TIME AS FUNCTION OF THE QUANTITY OF Pd CATALYST "A" ON $BaSO_4$.



1. See Table V/b.
2. See Table V/a.

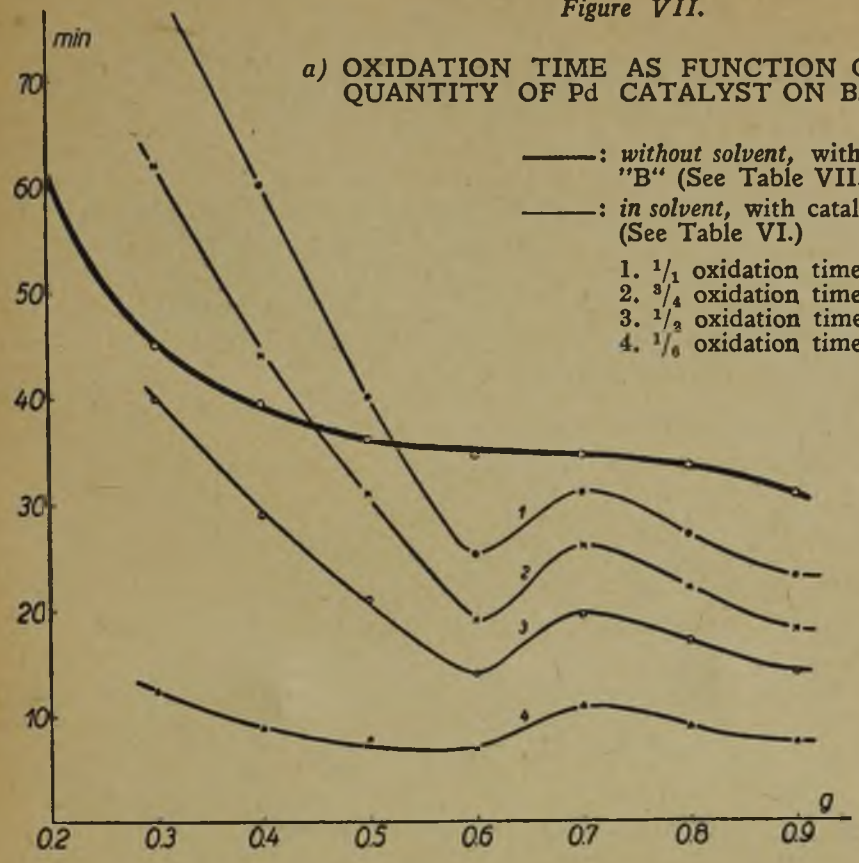
b) PERCENT OF O_2 CONSUMPTION TO FORM PERBENZOIC ACID AS FUNCTION OF THE QUANTITY OF Pd CATALYST "A" ON $BaSO_4$.



1. After absorption of $^1/_2$ mol O_2 (See Table V/b.)
2. After excess consumption (See Table V/a.)

Figure VII.

a) OXIDATION TIME AS FUNCTION OF THE QUANTITY OF Pd CATALYST ON $BaSO_4$.

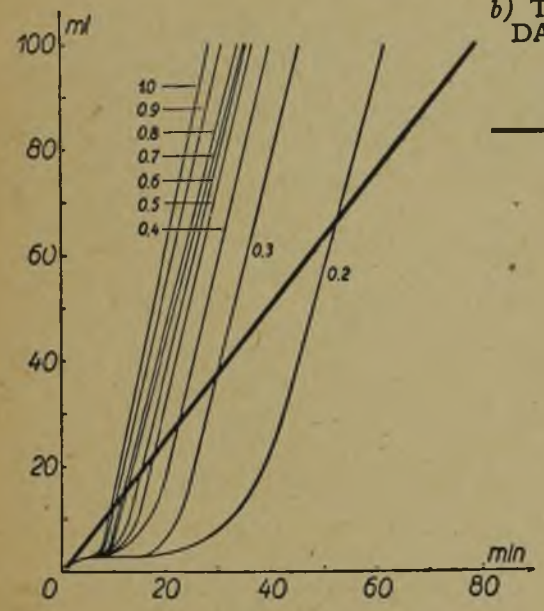


———: *without solvent,* with catalyst "B" (See Table VII.)

———: *in solvent,* with catalyst "C": (See Table VI.)

1. $^1/_1$ oxidation time
2. $^3/_4$ oxidation time
3. $^1/_2$ oxidation time
4. $^1/_6$ oxidation time

b) TIME REQUIRED FOR AUTOXIDATION WITH Pd CATALYST "B" ON $BaSO_4$ WITHOUT SOLVENT. (See Table VII.)



———: O_2 absorption of benzaldehyde without catalyst

0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 = catalyst employed in g.

Figure VIII.

OXIDATION TIME AS FUNCTION OF Pd CATALYST ON $BaSO_4$, unsupported and supported, in CCl_4.

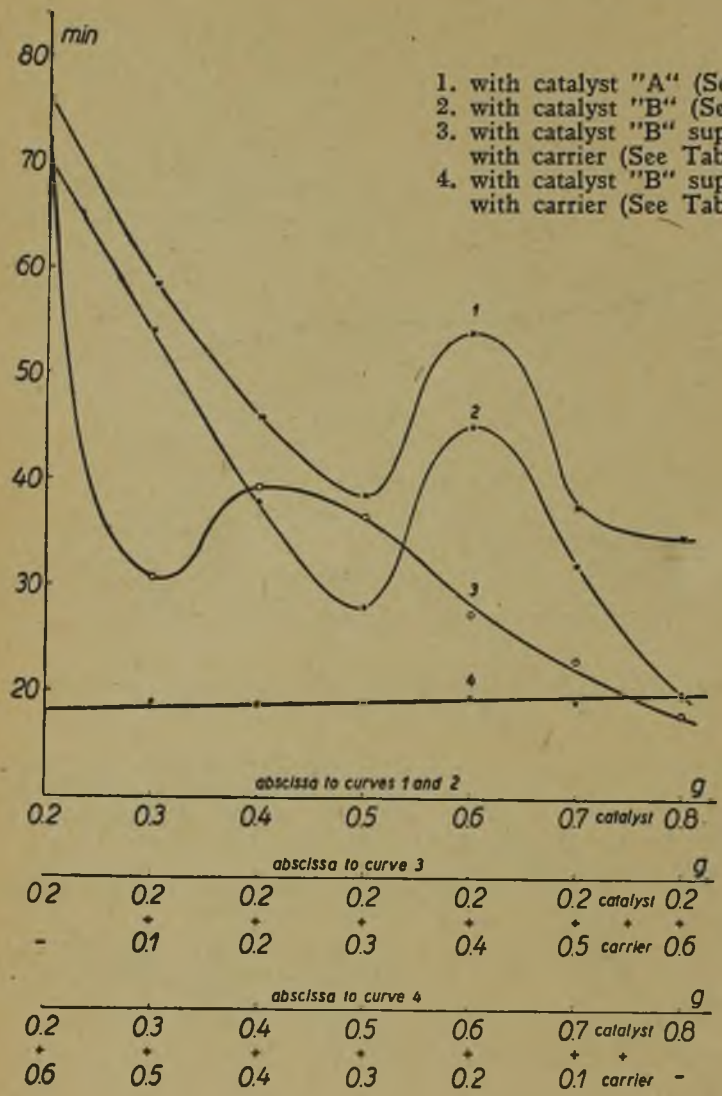
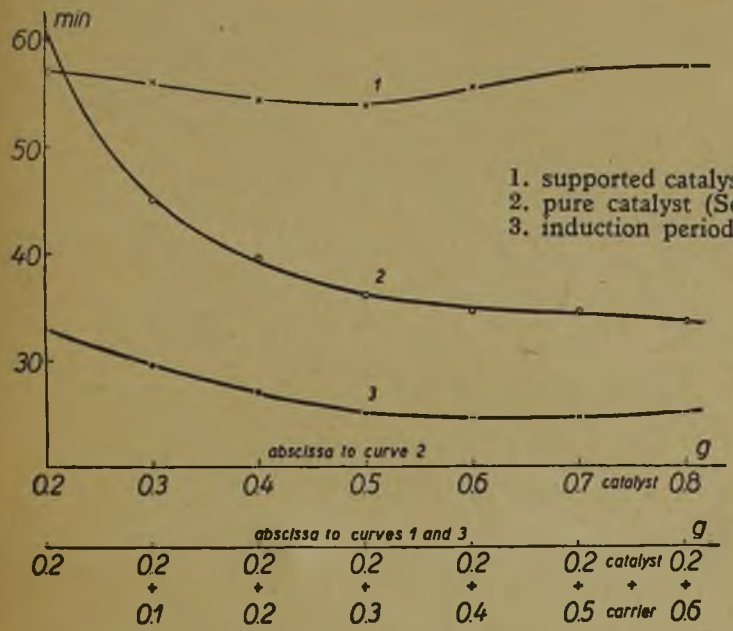
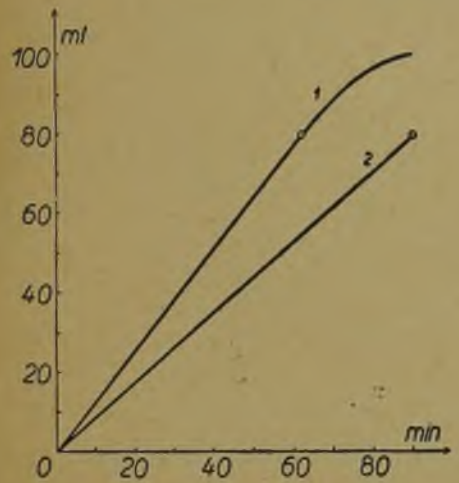


Figure IX.

a) TIME OF OXIDATION WITH PURE AND SUPPORTED CATALYST (Pd "B" on $BaSO_4$), without solvent.



b) INFLUENCE OF $BaSO_4$ ON AUTOXIDATION OF BENZALDEHYDE without solvent.
(See *Appendix* to Table IX/c.)



1. benzaldehyde, pure
2. benzaldehyde + $BaSO_4$

LITERATURE.

1. *C. Moureu* and *C. Duffraisse*, Compt. rend. *176*, 797 (1923).
2. *H. L. J. Bäckström*, J. Am. Chem. Soc. *49*, 1460 (1927).
3. *N. A. Milas*, J. Am. Chem. Soc. *52*, 739 (1930).
4. *E. Berl* and *K. Winnacker*, Ztschr. Phys. Chem. (A) *148*, 261 (1930).
5. *E. Raymond*, Journ. Chim. Phys. *28*, 316, 421, 480 (1931).
6. *M. Brunner*, Helv. Chim. Acta *10*, 707 (1927).
7. *Z. Csűrös, K. Zech* and *I. Géczy*, Hung. Acta Chim. *1*, 1 (1946).
8. *A. Buzágh* and *B. Molnár*, See *B. Molnár*, Dissertation, 1936, Budapest.
9. *F. Wöhler* and *J. Liebig*, Lieb. Ann. *3*, 253 (1832).
10. *C. F. Schönbein*, Journ. prakt. Chem. *74*, 328 (1858).
11. *C. Engler* and *W. Wild*, Ber. *30*, 1669 (1897).
12. *A. Baeyer* and *V. Villiger*, Ber. *33*, 1569 (1900).
13. *H. Staudinger*, Ber. *58*, 1075 (1925).
14. *H. J. Almquist* and *G. E. K. Branch*, J. Am. Chem. Soc. *54*, 2293 (1932).
15. *R. Kühn* and *K. Meyer*, Naturwiss. *16*, 1028 (1928).
16. *E. K. Rideal*, Rapport du Congres. Solway. 1925. (Cit. see 6.)
17. *O. M. Reiff*, J. Am. Chem. Soc. *48*, 2893 (1926).
18. *R. G. W. Norrish*, Journ. Chem. Soc. (London) *123*, 3006 (1923).
19. *C. Moureu, C. Duffraisse* and *M. Radoche*, Compt. Rend. *187*, 157 (1928).
20. *H. L. J. Bäckström*, Vetenskapsakad. Nobel Inst. *6*, 15, 16 (1927); Cit. See 5).
21. *C. Duffraisse* and *P. Chovin*, See *G.—M. Schwab*, Handb. der Katalyse II. 339.
22. *E. Briner*, Helv. Chim. Acta *14*, 794 (1931); *15*, 1227 (1932).
23. *H. S. Taylor*, J. Phys. Chem. *27*, 322 (1923); C. *1923. III.* 344.
24. *N. R. Dhar*, Ztschr. anorg. Chem. *139*, 194 (1924); C. *1924. II.* 2631; J. Phys. Chem. *28*, 948 (1924); C. *1924. II.* 2316.
25. *H. Wieland*, Ber. *45*, 2606 (1912).
26. *H. Wieland*, Ber. *54*, 2356 (1921).
27. *Z. Csűrös, K. Zech* and *T. Pfliegel*, Hung. Acta Chim. *1*, 24 (1946).
28. *Z. Csűrös* and *E. Gergely* née *Popper*, Hung. Acta Chim. Vol. *1*. (No. 4-5) 1-26 (1949); See *E. Popper*, Dissertation, Budapest, 1946.
29. *Z. Csűrös* and *I. Sellő*, Hung. Acta Chim. Vol. *1*. (No. 4-5) 27-44 (1949); See *I. Sellő*, Dissertation, Budapest, 1946.
30. *R. Willstätter* and *E. Waldschmidt—Leitz*, Ber. *54*, 113 (1921).
31. *A. Skita* and *W. A. Meyer*, Ber. *45*, 3585 (1912).
32. *L. Gattermann* and *H. Wieland*, Die Praxis des organischen Chemikers, (1943) 368.
33. *E. Schmidt*, Ber. *52*, 409 (1919).

A szerkesztésért és kiadásért dr. Csűrös Zoltán felelős.

50.323. — Egyetemi Nyomda NV., Budapest. (F.: Tirai Richárd.)

CONTENTS